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Rainer Dick

Advanced Quantum Mechanics

Materials and Photons

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With 62 Figures

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Preface

Quantum mechanics was invented in an era of intense and seminal scientific research between 1900 and 1928 (and in many regards continues to be developed and expanded) because neither the properties of atoms and electrons, nor the spectrum of radiation from heat sources could be explained by the classical theories of mechanics, electrodynamics and thermodynamics. It was a major intellectual achievement and a breakthrough of curiosity driven fundamental research which formed quantum theory into one of the pillars of our present understanding of the fundamental laws of nature. The properties and behavior of every elementary particle is governed by the laws of quantum theory. However, the rule of quantum mechanics is not limited to atomic and subatomic scales, but also affects macroscopic systems in a direct and profound manner. The electric and thermal conductivity properties of materials are determined by quantum effects, and the electromagnetic spectrum emitted by a star is primarily determined by the quantum properties of photons. It is therefore not surprising that quantum mechanics permeates all areas of research in advanced modern physics and materials science, and training in quantum mechanics plays a prominent role in the curriculum of every major physics or chemistry department.

The ubiquity of quantum effects in materials implies that quantum mechanics also evolved into a major tool for advanced technological research. The construction of the first nuclear reactor in Chicago in 1942 and the development of nuclear technology could not have happened without a proper understanding of the quantum properties of particles and nuclei. However, the real breakthrough for a wide recognition of the relevance of quantum effects in technology occured with the invention of the transistor in 1948 and the ensuing rapid development of semiconductor electronics. This proved once and for all the importance of quantum mechanics for the applied sciences and engineering, only 22 years after publication of the Schrödinger equation! Electronic devices like transistors rely heavily on the quantum mechanical emergence of energy bands in materials, which can be considered as a consequence of combination of many atomic orbitals or as a consequence of delocalized electron states probing a lattice structure. Today the rapid developments of spintronics, photonics and nanotechnology provide continuing testimony to the technological relevance of quantum mechanics.

As a consequence, every physicist, chemist and electrical engineer nowadays has to learn aspects of quantum mechanics, and we are witnessing a time

when also mechanical and aerospace engineers are advised to take at least a 2nd year course, due to the importance of quantum mechanics for elasticity and stability properties of materials. Furthermore, quantum information appears to become inceasingly relevant for computer science and information technology, and a whole new area of quantum technology will likely follow in the wake of this development. Therefore it seems safe to posit that within the next two generations, 2nd and 3rd year quantum mechanics courses will become as abundant and important in the curricula of science and engineering colleges as first and second year calculus courses.

Quantum mechanics continues to play a dominant role in particle physics and atomic physics - after all, the Standard Model of particle physics is a quantum theory, and the spectra and stability of atoms cannot be explained without quantum mechanics. However, most scientists and engineers use quantum mechanics in advanced materials research. Furthermore, the dominant interaction mechanisms in materials (beyond the nuclear level) are electromagnetic, and many experimental techniques in materials science are based on photon probes. The introduction to quantum mechanics in the present book takes this into account by including aspects of condensed matter theory and the theory of photons at earlier stages and to a larger extent than other quantum mechanics texts. Quantum properties of materials provide neat and very interesting illustrations of time-independent and time-dependent perturbation theory, and many students are better motivated to master the concepts of quantum mechanics when they are aware of the direct relevance for modern technology. A focus on the quantum mechanics of photons and materials is also perfectly suited to prepare students for future developments in quantum information technology, where entanglement of photons or spins, decoherence, and time evolution operators will be key concepts.

Other novel features of the discussion of quantum mechanics in this book concern attention to relevant mathematical aspects which otherwise can only be found in journal articles or mathematical monographs. Special appendices include a mathematically rigorous discussion of the completeness of Sturm-Liouville eigenfunctions in one spatial dimension, an evaluation of the Baker-Campbell-Hausdorff formula to higher orders, and a discussion of logarithms of matrices. Quantum mechanics has an extremely rich and beautiful mathematical structure. The growing prominence of quantum mechanics in the applied sciences and engineering has already reinvigorated increased research efforts on its mathematical aspects. Both students who study quantum mechanics for the sake of its numerous applications, as well as mathematically inclined students with a primary interest in the formal structure of the theory should therefore find this book interesting.

This book emerged from a quantum mechanics course which I had introduced at the University of Saskatchewan in 2001. It should be suitable both for advanced undergraduate and introductory graduate courses on the subject. To make advanced quantum mechanics accessible to wider audiences which might not have been exposed to standard second and third year courses on

atomic physics, analytical mechanics, and electrodynamics, important aspects of these topics are briefly, but concisely introduced in special chapters and appendices. The success and relevance of quantum mechanics has reached far beyond the realms of physics research, and physicists have a duty to disseminate the knowledge of quantum mechanics as widely as possible.

Saskatoon, Saskatchewan, Canada *Rainer Dick*

To the Students

Congratulations! You have reached a stage in your studies where the topics of your inquiry become ever more interesting and more relevant for modern research in basic science and technology.

Together with your professors, I will have the privilege to accompany you along the exciting road of your own discovery of the bizarre and beautiful world of quantum mechanics. I will aspire to share my own excitement that I continue to feel for the subject and for science in general.

You will be introduced to many analytical and technical skills that are used in everyday applications of quantum mechanics. These skills are essential in virtually every aspect of modern research. A proper understanding of a materials science measurement at a synchrotron requires a proper understanding of photons and quantum mechanical scattering, just like manipulation of qubits in quantum information research requires a proper understanding of spin and photons and entangled quantum states. Quantum mechanics is ubiquitous in modern research. It governs the formation of microfractures in materials, the conversion of light into chemical energy in chlorophyll or into electric impulses in our eyes, and the creation of particles at the Large Hadron Collider.

Technical mastery of the subject is of utmost importance for understanding quantum mechanics. Trying to decipher or apply quantum mechanics without knowing how it really works in the calculation of wave functions, energy levels, and cross sections is just idle talk, and always prone for misconceptions. Therefore we will go through a great many technicalities and calculations, because you and I (and your professor!) have a common goal: You should become an expert in quantum mechanics.

However, there is also another message in this book. The apparently exotic world of quantum mechanics is *our* world. Our bodies and all the world around us is built on quantum effects and ruled by quantum mechanics. It is not apparent and only visible to the *cognoscenti*. Therefore we have developed a mode of thought and explanation of the world that is based on classical pictures – mostly waves and particles in mechanical interaction. This mode of thought was sufficient for survivial of our species so far, and it culminated in a powerful tool called classical physics. However, by 1900 those who were paying attention had caught enough glimpses of the underlying non-classical world to embark on the exciting journey of discovering quantum mechanics. Indeed, every single atom in your body is ruled by the laws of quantum mechanics, and could not even exist as a classical particle. The electrons that provide the light for your

long nights of studying generate this light in stochastic quantum leaps from a state of a single electron to a state of an electron and a photon. And maybe the most striking example of all: There is *absolutely nothing classical* in the sunlight that provides the energy for all life on Earth.

Quantum theory is not a young theory any more. The scientific foundations of the subject were developed over half a century between 1900 and 1949, and many of the mathematical foundations were even developed in the 19th century. The steepest ascent in the development of quantum theory appeared between 1924 and 1928, when matrix mechanics, Schrödinger's equation, the Dirac equation and field quantization were invented. I have included numerous references to original papers from this period, not to ask you to read all those papers – after all, the primary purpose of a textbook is to put major achievements into context, provide an introductory overview at an appropriate level, and replace often indirect and circuitous original derivations with simpler explanations – but to honour the people who brought the then nascent theory to maturity. Quantum theory is an extremely well established and developed theory now, which has proven itself on numerous occasions. However, we still continue to improve our collective understanding of the theory and its wide ranging applications, and we test its predicitions and its probabilistic interpretation with ever increasing accuracy. The implications and applications of quantum mechanics are limitless, and we are witnessing a time when many technologies have reached their "quantum limit", which is a misnomer for the fact that any methods of classical physics are just useless in trying to describe or predict the behavior of atomic scale devices. It is a "limit" for those who do not want to learn quantum physics. For you, it holds the promise of excitement and opportunity if you are prepared to work hard and if you can understand the calculations.

Quantum mechanics combines power and beauty in a way that even supersedes advanced analytical mechanics and electrodynamics. Quantum mechanics is universal and therefore incredibly versatile, and if you have a sense for mathematical beauty: the structure of quantum mechanics is breathtaking, indeed.

I sincerely hope that reading this book will be an enjoyable and exciting experience for you.

To the Instructor

Dear Colleague,

as professors of quantum mechanics courses, we enjoy the privilege of teaching one of the most exciting subjects in the world. However, we often have to do this with fewer lecture hours than were available for the subject in the past, when at the same time we should include more material to prepare students for research or modern applications of quantum mechanics. Furthermore, students have become more mobile between universities (which is good) and between academic programs (which can have positive and negative implica-

tions). Therefore we are facing the task to teach an advanced subject to an increasingly heterogeneous student body with very different levels of preparation. Nowadays the audience in a fourth year undergraduate or beginning graduate course often includes students who have not gone through a course on Lagrangian mechanics, or have not seen the covariant formulation of electrodynamics in their electromagnetism courses. I deal with this problem by including one special lecture on each topic in my quantum mechanics course, and this is what Appendices A and B are for. I have also tried to be as inclusive as possible without sacrificing content or level of understanding by starting at a level that would correspond to an advanced second year Modern Physics or Quantum Chemistry course and then follow a steeply ascending route that takes the students all the way from Planck's law to the photon scattering tensor.

The selection and arrangement of topics in this book is determined by the desire to develop an advanced undergraduate and introductory gaduate level course that is useful to as many students as possible, in the sense of giving them a head start into major current research areas or modern applications of quantum mechanics without neglecting the necessary foundational training.

There is a core of knowledge that every student is expected to know by heart after having taken a course in quantum mechanics. Students must know the Schrödinger equation. They must know how to solve the harmonic oscillator and the Coulomb problem, and they must know how to extract information from the wave function. They should also be able to apply basic perturbation theory, and they should understand that a wave function $\langle \boldsymbol{x}|\psi(t)\rangle$ is only one particular representation of a quantum state $|\psi(t)\rangle$.

In a North American physics program, students would traditionally learn all these subjects in a 300-level Quantum Mechanics course. Here these subjects are discussed in Chapters 1-7 and 9. This allows the instructor to use this book also in 300-level courses or introduce those chapters in a 400-level or graduate course if needed. Depending on their specialization, there will be an increasing number of students from many different science and engineering programs who will have to learn these subjects at M.Sc. or beginning Ph.D. level before they can learn about photon scattering or quantum effects in materials, and catering to these students will also become an increasingly important part of the mandate of physics departments. Including chapters 1-7 and 9 with the book is part of the philosophy of being as inclusive as possible to disseminate knowledge in advanced quantum mechanics as widely as possible.

Additional training in quantum mechanics in the past traditionally focused on atomic and nuclear physics applications, and these are still very important topics in fundamental and applied science. However, a vast number of our current students in quantum mechanics will apply the subject in materials science in a broad sense encompassing condensed matter physics, chemistry and engineering. For these students it is beneficial to see Bloch's theorem, Wannier states, and basics of the theory of covalent bonding embedded with their quantum mechanics course. Another important topic for these students

is quantization of the Schrödinger field. Indeed, it is also useful for students in nuclear and particle physics to learn quantization of the Schrödinger field because it makes quantization of gauge fields and relativistic matter fields so much easier if they know quantum field theory in the non-relativistic setting.

Furthermore, many of our current students will use or manipulate photon probes in their future graduate and professional work. A proper discussion of photon-matter interactions is therefore also important for a modern quantum mechanics course. This should include minimal coupling, quantization of the Maxwell field, and applications of time-dependent perturbation theory for photon absorption, emission and scattering.

Students should also know the Klein-Gordon and Dirac equations after completion of their course, not only to understand that Schrödinger's equation is not the final answer in terms of wave equations for matter particles, but to understand the nature of relativistic corrections like Pauli or Rashba terms.

The scattering matrix is introduced as early as possible in terms of matrix elements of the time evolution operator on states in the interaction picture, $S_{fi}(t,t') = \langle f|U_D(t,t')|i\rangle$, cf. equation (13.20). This representation of the scattering matrix appears so naturally in ordinary time-dependent perturbation theory that it makes no sense to defer the notion of an S-matrix to the discussion of scattering in quantum field theory with two or more particles in the initial state. It actually mystifies the scattering matrix to defer its discussion until field quantization has been introduced. On the other hand, introducing the scattering matrix even earlier in the framework of scattering off static potentials is counterproductive, because its natural and useful definition as matrix elements of a time evolution operator cannot properly be introduced at that level, and the notion of the scattering matrix does not really help with the calculation of cross sections for scattering off static potentials.

I have also emphasized the discussion of the various roles of transition matrix elements depending on whether the initial or final states are discrete or continuous. It helps students to understand transition probabilities, decay rates, absorption cross sections and scattering cross sections if the discussion of these concepts is integrated in one chapter, cf. Chapter 13. Furthermore, I have put an emphasis on canonical field quantization. Path integrals provide a very elegant description for free-free scattering, but bound states and energy levels, and basic many-particle quantum phenomena like exchange holes are very efficiently described in the canonical formalism. Feynman rules also appear more intuitive in the canonical formalism of explicit particle creation and annihilation.

The core advanced topics in quantum mechanics that an instructor might want to cover in a traditional 400-level or introductory graduate course are included with Chapters 8, 11-13, 15-18, and 21. However, instructors of a more inclusive course for general science and engineering students should include materials from Chapters 1-7 and 9, as appropriate.

The direct integration of training in quantum mechanics with the foundations of condensed matter physics, field quantization, and quantum optics is very important for the advancement of science and technology. I hope that this book will help to achieve that goal. I would greatly appreciate your comments and criticism. Please send them to rainer.dick@usask.ca.

Contents

1 The Need for Quantum Mechanics **1**

1.1 Electromagnetic spectra and evidence for discrete energy levels . . . 1
1.2 Blackbody radiation and Planck's law . . . 3
1.3 Blackbody spectra and photon fluxes . . . 8
1.4 The photoelectric effect . . . 14
1.5 Wave-particle duality . . . 15
1.6 Why Schrödinger's equation? . . . 16
1.7 Interpretation of Schrödinger's wave function . . . 18
1.8 Problems . . . 22

2 Self-adjoint Operators and Eigenfunction Expansions **25**

2.1 The δ function and Fourier transforms . . . 25
2.2 Self-adjoint operators and completeness of eigenstates . . . 30
2.3 Problems . . . 33

3 Simple Model Systems **35**

3.1 Barriers in quantum mechanics . . . 35
3.2 Quantum wells, quantum wires and quantum dots . . . 42
3.3 The attractive δ function potential . . . 45
3.4 Evolution of free Schrödinger wave packets . . . 47
3.5 Problems . . . 52

4 Notions from Linear Algebra and Bra-Ket Notation **57**

4.1 Notions from linear algebra . . . 58
4.2 Bra-ket notation in quantum mechanics . . . 66
4.3 The adjoint Schrödinger equation and the virial theorem . . . 70
4.4 Problems . . . 72

5 Formal Developments **75**

5.1 Uncertainty relations . . . 75
5.2 Energy representation . . . 79
5.3 Dimensions of states . . . 81
5.4 Gradients and Laplace operators in general coordinate systems . 82

5.5 Separation of differential equations . . . 86
5.6 Problems . . . 88

6 Harmonic Oscillators and Coherent States 91
6.1 Basic aspects of harmonic oscillators . . . 91
6.2 Solution of the harmonic oscillator by the operator method . . . 92
6.3 Construction of the states in the x-representation . . . 94
6.4 Lemmata for exponentials of operators . . . 96
6.5 Coherent states . . . 98
6.6 Problems . . . 104

7 Central Forces in Quantum Mechanics 107
7.1 Separation of center of mass motion and relative motion . . . 107
7.2 The concept of symmetry groups . . . 110
7.3 Operators for kinetic energy and angular momentum . . . 111
7.4 Defining representation of the three-dimensional rotation group 113
7.5 Matrix representations of the rotation group . . . 114
7.6 Construction of the spherical harmonic functions . . . 116
7.7 Basic features of motion in central potentials . . . 120
7.8 Free spherical waves: the free particle with sharp M_z, M^2 . . . 121
7.9 Bound energy eigenstates of the hydrogen atom . . . 124
7.10 Spherical Coulomb waves . . . 131
7.11 Problems . . . 135

8 Spin and Addition of Angular Momentum Type Operators 139
8.1 Spin and magnetic dipole interactions . . . 139
8.2 Transformation of wave functions under rotations . . . 142
8.3 Addition of angular momentum like quantities . . . 144
8.4 Problems . . . 150

9 Stationary Perturbations in Quantum Mechanics 151
9.1 Time-independent perturbation theory without degeneracies . . . 151
9.2 Time-independent perturbation theory with degeneracies . . . 156
9.3 Problems . . . 161

10 Quantum Aspects of Materials I 163
10.1 Bloch's theorem . . . 163
10.2 Wannier states . . . 166
10.3 Time-dependent Wannier states . . . 169
10.4 The Kronig-Penney model . . . 170
10.5 kp perturbation theory and effective mass . . . 174
10.6 Problems . . . 176

11 Scattering Off Potentials **183**
11.1 The free energy dependent Green's function . . . 185
11.2 Potential scattering in the Born approximation . . . 187
11.3 Scattering off a hard sphere . . . 190
11.4 Rutherford scattering . . . 194
11.5 Problems . . . 198

12 The Density of States **199**
12.1 Counting of oscillation modes . . . 200
12.2 The continuum limit . . . 202
12.3 Density of states per unit of energy . . . 204
12.4 Density of states in radiation . . . 205
12.5 Problems . . . 207

13 Time-dependent Perturbations in Quantum Mechanics **209**
13.1 Pictures of quantum dynamics . . . 209
13.2 The Dirac picture . . . 215
13.3 Transitions between discrete states . . . 218
13.4 Transitions from discrete states into continuous states . . . 223
13.5 Transitions from continuous states into discrete states . . . 230
13.6 Transitions between continuous states – scattering . . . 232
13.7 Expansion of the scattering matrix to higher orders . . . 237
13.8 Problems . . . 238

14 Path Integrals in Quantum Mechanics **241**
14.1 Time evolution in the path integral formulation . . . 242
14.2 Path integrals in scattering theory . . . 247
14.3 Problems . . . 254

15 Coupling to Electromagnetic Fields **255**
15.1 Electromagnetic couplings . . . 255
15.2 Stark effect and static polarizability tensors . . . 261
15.3 Dynamical polarizability tensors . . . 263
15.4 Problems . . . 270

16 Principles of Lagrangian Field Theory **273**
16.1 Lagrangian field theory . . . 273
16.2 Symmetries and conservation laws . . . 276
16.3 Problems . . . 280

17 Non-relativistic Quantum Field Theory **283**
17.1 Quantization of the Schrödinger field . . . 284
17.2 Time evolution for time-dependent Hamiltonians . . . 291
17.3 The connection between first and second quantized theory . . . 292
17.4 The Dirac picture in quantum field theory . . . 296
17.5 Inclusion of spin . . . 299

17.6 Two-particle interaction potentials and equations of motion . . . 303
17.7 Expectation values and exchange terms . . . 307
17.8 From many particle theory to second quantization . . . 309
17.9 Problems . . . 311

18 Quantization of the Maxwell Field: Photons 321
18.1 Lagrange density and mode expansion for the Maxwell field . . . 321
18.2 Photons . . . 327
18.3 Coherent states of the electromagnetic field . . . 329
18.4 Photon coupling to relative motion . . . 330
18.5 Photon emission rates . . . 331
18.6 Photon absorption . . . 339
18.7 Stimulated emission of photons . . . 342
18.8 Photon scattering . . . 344
18.9 Problems . . . 352

19 Quantum Aspects of Materials II 355
19.1 The Born-Oppenheimer approximation . . . 356
19.2 Covalent bonding . . . 359
19.3 Bloch and Wannier operators . . . 368
19.4 The Hubbard model . . . 372
19.5 Vibrations in molecules and lattices . . . 374
19.6 Quantized lattice vibrations – phonons . . . 385
19.7 Electron-phonon interactions . . . 389
19.8 Problems . . . 393

20 Dimensional Effects in Low-dimensional Systems 397
20.1 Quantum mechanics in d dimensions . . . 397
20.2 Inter-dimensional effects in interfaces and thin layers . . . 403
20.3 Problems . . . 408

21 Klein-Gordon and Dirac Fields 413
21.1 The Klein-Gordon equation . . . 413
21.2 Klein's paradox . . . 419
21.3 The Dirac equation . . . 423
21.4 Energy-momentum tensor for quantum electrodynamics . . . 429
21.5 The non-relativistic limit of the Dirac equation . . . 433
21.6 Two-particle scattering cross sections . . . 435
21.7 Photon scattering by free electrons . . . 440
21.8 Møller scattering . . . 450
21.9 Problems . . . 458

Appendix A: Lagrangian Mechanics 461

Appendix B: The Covariant Formulation of Electrodynamics 467

Appendix C: Completeness of Sturm-Liouville Eigenfunctions **483**

Appendix D: Properties of Hermite Polynomials **497**

Appendix E: The Baker-Campbell-Hausdorff Formula **499**

Appendix F: The Logarithm of a Matrix **503**

Appendix G: Dirac γ matrices **507**

Appendix H: Spinor representations of the Lorentz group **517**

Appendix I: Green's functions in d dimensions **525**

Bibliography **543**

Index **547**

Chapter 1

The Need for Quantum Mechanics

1.1 Electromagnetic spectra and evidence for discrete energy levels

Quantum mechanics was initially invented because classical mechanics, thermodynamics and electrodynamics provided no means to explain the properties of atoms, electrons, and electromagnetic radiation. Furthermore, it became clear after the introduction of Schrödinger's equation and the quantization of Maxwell's equations that we cannot explain *any* physical property of matter and radiation without the use of quantum theory. We will see a lot of evidence for this in the following chapters. However, in the present chapter we will briefly and selectively review the early experimental observations and developments which led to the development of quantum mechanics over a period of intense research between 1900 and 1928.

The first evidence that classical physics was incomplete appeared in unexpected properties of electromagnetic spectra. Thin gases of atoms or molecules emit line spectra which contradict the fact that a classical system of electric charges can oscillate at any frequency, and therefore can emit radiation of any frequency. This was a major scientific puzzle from the 1850s until the inception of the Schrödinger equation in 1926.

Contrary to a thin gas, a hot body does emit a continuous spectrum, but even those spectra were still puzzling because the shape of heat radiation spectra could not be explained by classical thermodynamics and electrodynamics. In fact, classical physics provided no means at all to predict any sensible shape for the spectrum of a heat source! But at last, hot bodies do emit a continuous spectrum and therefore, from a classical point of view, their spectra are not quite as strange and unexpected as line spectra. It is therefore not surprising that the first real clues for a solution to the puzzles of electromagnetic spectra emerged when Max Planck figured out a way to calculate the spectra of heat sources under the simple, but classically extremely counterintuitive assumption

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that the energy in heat radiation of frequency f is *quantized* in integer multiples of a minimal energy quantum hf,

$$E = nhf, \quad n \in \mathbb{N}. \tag{1.1}$$

The constant h that Planck had introduced to formulate this equation became known as Planck's constant and it could be measured from the shape of heat radiation spectra. A modern value is $h = 6.626 \times 10^{-34}\,\mathrm{J \cdot s} = 4.136 \times 10^{-15}\,\mathrm{eV \cdot s}$. We will review the puzzle of heat radiation and Planck's solution in the next section, because Planck's calculation is instructive and important for the understanding of incandescent light sources and it illustrates in a simple way how quantization of energy levels yields results which are radically different from predictions of classical physics.

Albert Einstein then pointed out that equation (1.1) also explains the photoelectric effect. He also proposed that Planck's quantization condition is not a property of any particular mechanism for generation of electromagnetic waves, but an intrinsic property of electromagnetic waves. However, once equation (1.1) is accepted as an intrinsic property of electromagnetic waves, it is a small step to make the connection with line spectra of atoms and molecules and conclude that these line spectra imply existence of discrete energy levels in atoms and molecules. Somehow atoms and molecules seem to be able to emit radiation only by jumping from one discrete energy state into a lower discrete energy state. This line of reasoning, combined with classical dynamics between electrons and nuclei in atoms then naturally leads to the Bohr-Sommerfeld theory of atomic structure. This became known as *old quantum theory.*

Apparently, the property which underlies both the heat radiation puzzle and the puzzle of line spectra is discreteness of energy levels in atoms, molecules, and electromagnetic radiation. Therefore, *one major motivation for the development of quantum mechanics was to explain discrete energy levels in atoms, molecules, and electromagnetic radiation.*

It was Schrödinger's merit to find an explanation for the discreteness of energy levels in atoms and molecules through his wave equation[1] ($\hbar \equiv h/2\pi$)

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\psi(\boldsymbol{x}, t) = -\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{x}, t) + V(\boldsymbol{x})\psi(\boldsymbol{x}, t). \tag{1.2}$$

A large part of this book will be dedicated to the discussion of Schrödinger's equation. An intuitive motivation for this equation will be given in Section 1.6. Ironically, the fundamental energy quantization condition (1.1) for electromagnetic waves, which precedes the realization of discrete energy levels in atoms and molecules, cannot be derived by solving a wave equation, but emerges from the quantization of Maxwell's equations. This is at the heart of understanding photons and the quantum theory of electromagnetic waves. We will revisit this issue in Chapter 18. However, we can and will discuss already now the early quantum theory of the photon and what it means for the interpretation of spectra from incandescent sources.

[1] E. Schrödinger, Annalen Phys. 386, 109 (1926).

1.2 Blackbody radiation and Planck's law

Historically, Planck's deciphering of the spectra of incandescent heat and light sources played a key role for the development of quantum mechanics, because it included the first proposal of energy quanta, and it implied that line spectra are a manifestation of energy quantization in atoms and molecules. Planck's radiation law is also extremely important in astrophysics and in the technology of heat and light sources.

Generically, the heat radiation from an incandescent source is contaminated with radiation reflected from the source. Pure heat radiation can therefore only be observed from a non-reflecting, i.e. perfectly black body. Hence the name blackbody radiation for pure heat radiation. Physicists in the late 19th century recognized that the best experimental realization of a black body is a hole in a cavity wall. If the cavity is kept at temperature T, the hole will emit perfect heat radiation without contamination from any reflected radiation.

Suppose we have a heat radiation source (or thermal emitter) at temperature T. The power per area radiated from a thermal emitter at temperature T is denoted as its *exitance* (or *emittance*) $e(T)$. In the blackbody experiments $e(T) \cdot A$ is the energy per time leaking through a hole of area A in a cavity wall.

To calculate $e(T)$ as a function of the temperature T, as a first step we need to find out how it is related to the density $u(T)$ of energy stored in the heat radiation. One half of the radiation will have a velocity component towards the hole, because all the radiation which moves under an angle $\vartheta \leq \pi/2$ relative to the axis going through the hole will have a velocity component $v(\vartheta) = c\cos\vartheta$ in the direction of the hole. To find out the average speed v of the radiation in the direction of the hole, we have to average $c\cos\vartheta$ over the solid angle $\Omega = 2\pi\,\mathrm{sr}$ of the forward direction $0 \leq \varphi \leq 2\pi$, $0 \leq \vartheta \leq \pi/2$:

$$v = \frac{c}{2\pi}\int_0^{2\pi} d\varphi \int_0^{\pi/2} d\vartheta\, \sin\vartheta\cos\vartheta = \frac{c}{2}.$$

The effective energy current density towards the hole is energy density moving in forward direction $\times$ average speed in forward direction:

$$\frac{u(T)}{2}\frac{c}{2} = u(T)\frac{c}{4},$$

and during the time t an amount of energy

$$E = u(T)\frac{c}{4}tA$$

will escape through the hole. Therefore the emitted power per area $E/(tA) = e(T)$ is

$$e(T) = u(T)\frac{c}{4}. \tag{1.3}$$

However, Planck's radiation law is concerned with the *spectral exitance* $e(f,T)$, which is defined in such a way that

$$e_{[f_1,f_2]}(T) = \int_{f_1}^{f_2} df\, e(f,T)$$

is the power per area emitted in radiation with frequencies $f_1 \leq f \leq f_2$. In particular, the total exitance is

$$e(T) = e_{[0,\infty]}(T) = \int_0^\infty df\, e(f,T).$$

Operationally, the spectral exitance is the power per area emitted with frequencies $f \leq f' \leq f + \Delta f$, and normalized by the width Δf of the frequency interval,

$$e(f,T) = \lim_{\Delta f \to 0} \frac{e_{[f,f+\Delta f]}(T)}{\Delta f} = \lim_{\Delta f \to 0} \frac{e_{[0,f+\Delta f]} - e_{[0,f]}(T)}{\Delta f} = \frac{\partial}{\partial f} e_{[0,f]}(T).$$

The spectral exitance $e(f,T)$ can also be denoted as the *emitted power per area and per unit of frequency* or as the *spectral exitance in the frequency scale*.
The spectral energy density $u(f,T)$ is defined in the same way. If we measure the energy density $u_{[f,f+\Delta f]}(T)$ in radiation with frequency between f and $f+\Delta f$, then the energy per volume and per unit of frequency (i.e. the spectral energy density in the frequency scale) is

$$u(f,T) = \lim_{\Delta f \to 0} \frac{u_{[f,f+\Delta f]}(T)}{\Delta f} = \frac{\partial}{\partial f} u_{[0,f]}(T), \tag{1.4}$$

and the total energy density in radiation is

$$u(T) = \int_0^\infty df\, u(f,T).$$

The equation $e(T) = u(T)c/4$ also applies separately in each frequency interval $[f, f+\Delta f]$, and therefore must also hold for the corresponding spectral densities,

$$e(f,T) = u(f,T)\frac{c}{4}. \tag{1.5}$$

The following facts were known before Planck's work in 1900.
• The prediction from classical thermodynamics for the spectral exitance $e(f,T)$ (Rayleigh-Jeans law) was wrong, and actually non-sensible!
• The exitance $e(T)$ satisfies Stefan's law (Stefan, 1879; Boltzmann, 1884)

$$e(T) = \sigma T^4,$$

with the Stefan-Boltzmann constant

$$\sigma = 5.6704 \times 10^{-8}\, \frac{\mathrm{W}}{\mathrm{m^2 K^4}}.$$

• The spectral exitance $e(\lambda, T) = e(f, T)\Big|_{f=c/\lambda} \cdot c/\lambda^2$ per unit of wavelength (i.e. *the spectral exitance in the wavelength scale*) has a maximum at a wavelength

$$\lambda_{max} \cdot T = 2.898 \times 10^{-3}\,\mathrm{m} \cdot \mathrm{K} = 2898\,\mu\mathrm{m} \cdot \mathrm{K}.$$

This is Wien's displacement law (Wien, 1893).
The puzzle was to explain the observed curves $e(f, T)$ and to explain why classical thermodynamics had failed. We will explore these questions through a calculation of the spectral energy density $u(f, T)$. Equation (1.5) then also yields $e(f, T)$.
The key observation for the calculation of $u(f, T)$ is to realize that $u(f, T)$ can be split into two factors. If we want to know the radiation energy density $u_{[f,f+df]} = u(f, T)df$ in the small frequency interval $[f, f + df]$, then we can first ask ourselves how many different electromagnetic oscillation modes per volume, $g(f)df$, exist in that frequency interval. Each oscillation mode will then contribute an energy $\langle E\rangle(f, T)$ to the radiation energy density, where $\langle E\rangle(f, T)$ is the expectation value of energy in an electromagnetic oscillation mode of frequency f at temperature T,

$$u(f, T)df = g(f)df\langle E\rangle(f, T).$$

The spectal energy density $u(f, T)$ can therefore be calculated in two steps:
1. Calculate the number $g(f)$ of oscillation modes per volume and per unit of frequency ("counting of oscillation modes").
2. Calculate the mean energy $\langle E\rangle(f, T)$ in an oscillation of frequency f at temperature T.
The results can then be combined to yield the spectral energy density $u(f, T) = g(f)\langle E\rangle(f, T)$.
The number of electromagnetic oscillation modes per volume and per unit of frequency is an important quantity in quantum mechanics and will be calculated explicitly in Chapter 13, with the result

$$g(f) = \frac{8\pi f^2}{c^3}. \tag{1.6}$$

The corresponding density of oscillation modes in the wavelength scale is

$$g(\lambda) = g(f)\Big|_{f=c/\lambda} \cdot \frac{c}{\lambda^2} = \frac{8\pi}{\lambda^4}.$$

Statistical physics predicts that the probability $P_T(E)$ to find an oscillation of energy E in a system at temperature T should be exponentially suppressed,

$$P_T(E) = \frac{1}{k_B T} \exp\left(-\frac{E}{k_B T}\right). \tag{1.7}$$

The possible values of E are not restricted in classical physics, but can vary continuously between $0 \le E < \infty$. For example, for any classical oscillation

with fixed frequency f, continually increasing the amplitude yields a continuous increase in energy. The mean energy of an oscillation at temperature T according to classical thermodynamics is therefore

$$\langle E\rangle\Big|_{classical} = \int_0^\infty dE\, E P_T(E) = \int_0^\infty dE\, \frac{E}{k_B T} \exp\left(-\frac{E}{k_B T}\right) = k_B T. \quad (1.8)$$

Therefore the spectral energy density in blackbody radiation and the corresponding spectral exitance according to classical thermodynamics should be

$$u(f,t) = g(f) k_B T = \frac{8\pi f^2}{c^3} k_B T, \quad e(f,T) = u(f,T)\frac{c}{4} = \frac{2\pi f^2}{c^2} k_B T,$$

but this is obviously nonsensical: it would predict that every heat source should emit a diverging amount of energy at high frequencies/short wavelengths! This is the *ultraviolet catastrophe* of the Rayleigh-Jeans law.
Max Planck observed in 1900 that he could derive an equation which matches the spectra of heat sources perfectly if he assumes that the energy in electromagnetic waves of frequency f is quantized in multiples of the frequency,

$$E = nhf = n\frac{hc}{\lambda}, \quad n \in \mathbb{N}.$$

The exponential suppression of high energy oscillations then reads

$$P_T(E) = P_T(n) \propto \exp\left(-\frac{nhf}{k_B T}\right),$$

but due to the discreteness of the *energy quanta* hf, the normalized probabilities are now

$$\begin{aligned} P_T(E) = P_T(n) &= \left[1 - \exp\left(-\frac{hf}{k_B T}\right)\right] \exp\left(-\frac{nhf}{k_B T}\right) \\ &= \exp\left(-n\frac{hf}{k_B T}\right) - \exp\left(-(n+1)\frac{hf}{k_B T}\right), \end{aligned}$$

such that $\sum_{n=0}^\infty P_T(n) = 1$.
The resulting mean energy per oscillation mode is

$$\begin{aligned} \langle E\rangle &= \sum_{n=0}^\infty nhf P_T(n) \\ &= \sum_{n=0}^\infty nhf \exp\left(-n\frac{hf}{k_B T}\right) - \sum_{n=0}^\infty nhf \exp\left(-(n+1)\frac{hf}{k_B T}\right) \\ &= \sum_{n=0}^\infty nhf \exp\left(-n\frac{hf}{k_B T}\right) - \sum_{n=0}^\infty (n+1)hf \exp\left(-(n+1)\frac{hf}{k_B T}\right) \\ &\quad + hf \sum_{n=0}^\infty \exp\left(-(n+1)\frac{hf}{k_B T}\right) \end{aligned}$$

The first two sums cancel, and the last term yields the mean energy in an electromagnetic wave of frequency f at temperature T as

$$\langle E\rangle(f,T) = hf\frac{\exp\left(-\frac{hf}{k_BT}\right)}{1-\exp\left(-\frac{hf}{k_BT}\right)} = \frac{hf}{\exp\left(\frac{hf}{k_BT}\right)-1}. \tag{1.9}$$

Combination with $g(f)$ from equation (1.6) yields Planck's formulas for the spectral energy density and spectral exitance in heat radiation,

$$u(f,T) = \frac{8\pi hf^3}{c^3}\frac{1}{\exp\left(\frac{hf}{k_BT}\right)-1}, \quad e(f,T) = \frac{2\pi hf^3}{c^2}\frac{1}{\exp\left(\frac{hf}{k_BT}\right)-1}. \tag{1.10}$$

These functions fitted the observed spectra perfectly! The spectrum $e(f,T)$ and the emitted power $e_{[0,f]}(T)$ with maximal frequency f are displayed for $T = 5780$ K in Figures 1.1 and 1.2.

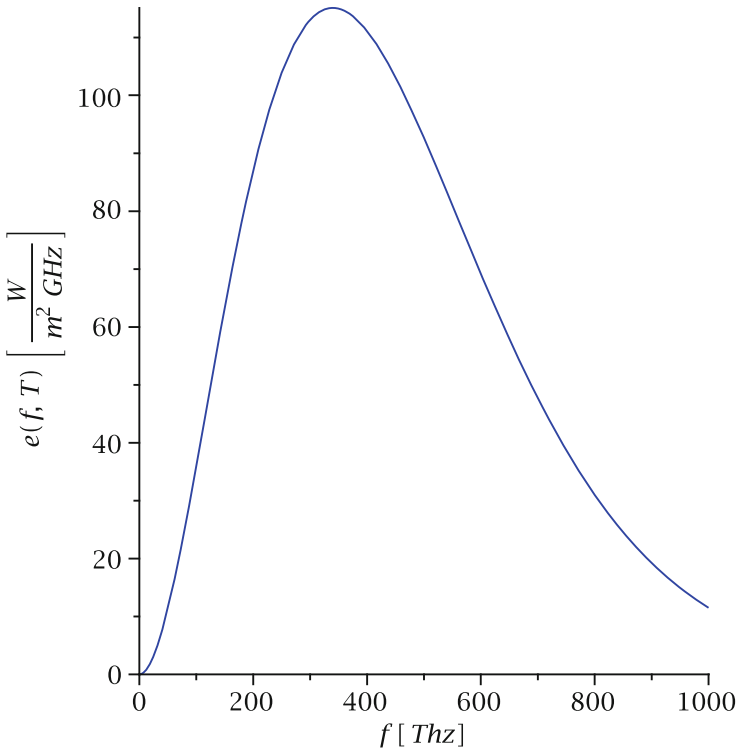


Figure 1.1: The spectral emittance $e(f,T)$ for a heat source of temperature $T = 5780$ K.

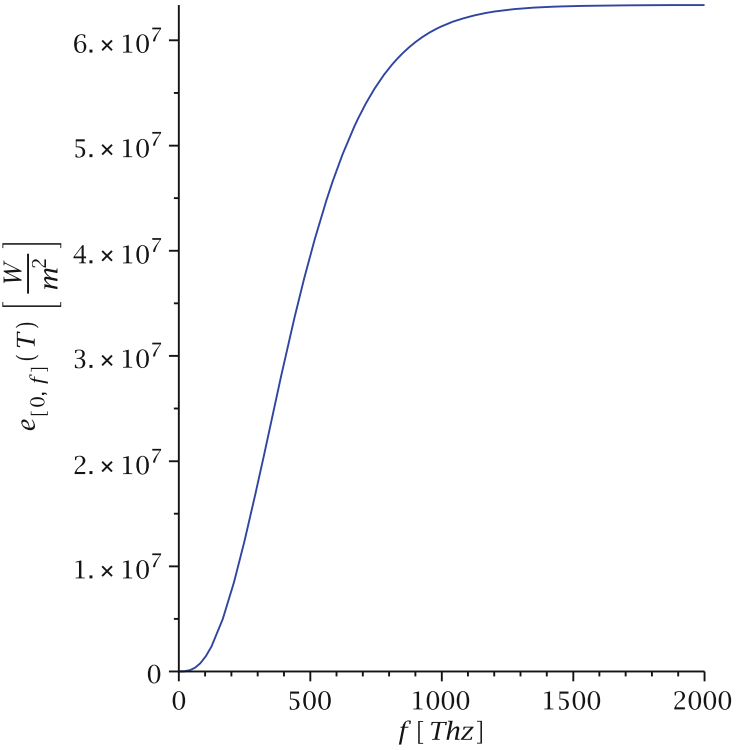


Figure 1.2: The emittance $e_{[0,f]}(T) = \int_0^f df'\, e(f', T)$ (i.e. emitted power per area in radiation with maximal frequency f) for a heat source of temperature $T = 5780$ K. The asymptote for $f \to \infty$ is $e_{[0,\infty]}(T) \equiv e(T) = \sigma T^4 = 6.33 \times 10^7\,\mathrm{W/m^2}$ for the temperature $T = 5780$ K.

1.3 Blackbody spectra and photon fluxes

Their technical relevance for the quantitative analysis of incandescent light sources makes it worthwhile to take a closer look at blackbody spectra. Blackbody spectra are also helpful to elucidate the notion of spectra more closely, and to explain that a maximum in a spectrum strongly depends on the choice of independent variable (e.g. wavelength or frequency) and dependent variable (e.g. energy flux or photon flux). In particular, it is sometimes claimed that our sun has maximal radiation output at a wavelength $\lambda_{\max} \simeq 500$ nm. This statement is actually very misleading if the notion of "radiation output" is not clearly defined, and if no explanation is included that different perfectly suitable notions of radiation output yield very different wavelengths or frequencies of maximal emission. We will see below that the statement above only applies to *maximal power output per unit of wavelength*, i.e. if we use a monochromator which slices the *wavelength* axis into intervals of equal length $d\lambda = c|df|/f^2$,

then we find maximal power output in an interval around $\lambda_{max} \simeq 500$ nm. However, we will also see that if we use a monochromator which slices the *frequency* axis into intervals of equal length $df = c|d\lambda|/\lambda^2$, then we find maximal power output in an interval around $f_{max} \simeq 340$ THz, corresponding to a wavelength $c/f_{\max} \simeq 880$ nm. If we ask for maximal photon counts instead of maximal power output, we find yet other values for peaks in the spectra.
Since Planck's radiation law (1.10) yielded perfect matches to observed blackbody spectra, it must also imply Stefan's law and Wien's law. Stefan's law is readily derived in the following way. The emitted power per area is

$$e(T) = \int_0^\infty df\, e(f,T) = \int_0^\infty d\lambda\, e(\lambda,T) = 2\pi\frac{k_B^4 T^4}{h^3c^2}\int_0^\infty dx\,\frac{x^3}{\exp(x)-1}.$$

Evaluation of the integral

$$\begin{aligned}\int_0^\infty dx\,\frac{x^3}{\exp(x)-1} &= \int_0^\infty dx\, x^3 \sum_{n=0}^\infty \exp[-(n+1)x] \\ &= -\sum_{n=1}^\infty \frac{d^3}{dn^3}\int_0^\infty dx\,\exp(-nx) = -\sum_{n=1}^\infty \frac{d^3}{dn^3}\frac{1}{n} \\ &= \sum_{n=1}^\infty \frac{6}{n^4} = 6\zeta(4) = \frac{\pi^4}{15}\end{aligned}$$

implies

$$e(T) = \frac{2\pi^5 k_B^4}{15h^3c^2}T^4,$$

i.e. Planck's law implied a prediction for the Stefan-Boltzmann constant in terms of the Planck constant h, which could be determined previously from a fit to the spectra,

$$\sigma = \frac{2\pi^5 k_B^4}{15h^3c^2}.$$

An energy flux $e(T) = 6.33 \times 10^7\,\mathrm{W/m^2}$ from the Sun yields a remnant energy flux at Earth's orbit of magnitude $e(T) \times (R_\odot/r_\oplus)^2 = 1.37\,\mathrm{kW/m^2}$. Here $R_\odot = 6.955 \times 10^8$ m is the radius of the Sun and $r_\oplus = 1.496 \times 10^{11}$ m is the radius of Earth's orbit.
For the derivation of Wien's law, we set

$$x = \frac{hc}{\lambda k_B T} = \frac{hf}{k_B T}.$$

Then we have with $e(\lambda,T) = e(f,T)|_{f=c/\lambda}c/\lambda^2$,

$$\begin{aligned}\frac{\partial}{\partial\lambda}e(\lambda,T) &= \frac{2\pi hc^2}{\lambda^5}\frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right)-1}\left(\frac{hc}{\lambda^2 k_B T}\frac{\exp\left(\frac{hc}{\lambda k_B T}\right)}{\exp\left(\frac{hc}{\lambda k_B T}\right)-1} - \frac{5}{\lambda}\right) \\ &= \frac{2\pi hc^2}{\lambda^6}\frac{1}{\exp(x)-1}\left(x\frac{\exp(x)}{\exp(x)-1} - 5\right),\end{aligned}$$

which implies that $\partial e(\lambda, T)/\partial\lambda = 0$ is satisfied if and only if

$$\exp(x) = \frac{5}{5 - x}.$$

This condition yields $x \simeq 4.965$. The wavelength of maximal spectral emittance $e(\lambda, T)$ therefore satisfies

$$\lambda_{\max} \cdot T \simeq \frac{hc}{4.965 k_B} = 2898\,\mu\mathrm{m} \cdot \mathrm{K}.$$

For a heat source of temperature $T = 5780$ K, like the surface of our sun, this yields (see Figure 1.3)

$$\lambda_{\max} = 501\,\mathrm{nm}, \quad \frac{c}{\lambda_{\max}} = 598\,\mathrm{THz}.$$

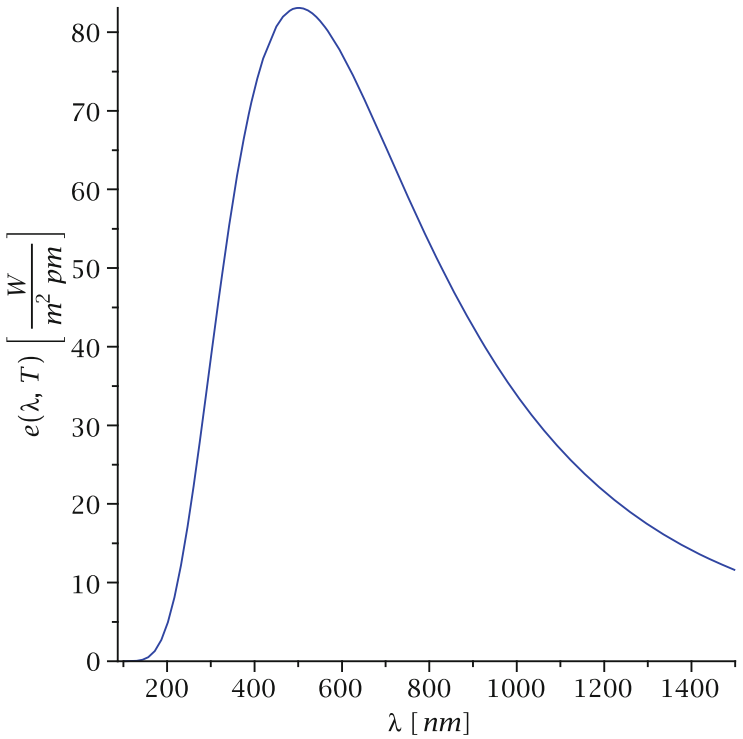


Figure 1.3: The spectral emittance $e(\lambda, T)$ for a heat source of temperature $T = 5780$ K.

One can also derive an analogue of Wien's law for the frequency $f_{\max}$ of maximal

spectral emittance $e(f,T)$. We have

$$\frac{\partial}{\partial f}e(f,T) = \frac{2\pi h f^2}{c^2}\frac{1}{\exp\left(\frac{hf}{k_BT}\right)-1}\left(3-\frac{hf}{k_BT}\frac{\exp\left(\frac{hc}{\lambda k_BT}\right)}{\exp\left(\frac{hc}{\lambda k_BT}\right)-1}\right)$$
$$= \frac{2\pi h f^2}{c^2}\frac{1}{\exp(x)-1}\left(3-x\frac{\exp(x)}{\exp(x)-1}\right),$$

which implies that $\partial e(f,T)/\partial f = 0$ is satisfied if and only if

$$\exp(x) = \frac{3}{3-x},$$

with solution $x \simeq 2.821$. The frequency of maximal spectral emittance $e(f,T)$ therefore satisfies

$$\frac{f_{\max}}{T} \simeq 2.821\frac{k_B}{h} = 58.79\,\frac{\mathrm{GHz}}{\mathrm{K}}.$$

This yields for a heat source of temperature $T = 5780$ K, as in Figure 1.1,

$$f_{\max} = 340\,\mathrm{THz}, \quad \frac{c}{f_{\max}} = 882\,\mathrm{nm}.$$

The photon fluxes in the wavelength scale and in the frequency scale, $j(\lambda,T)$ and $j(f,T)$, are defined below. The spectral emittance per unit of frequency, $e(f,T)$, is directly related to the photon flux per fractional wavelength or frequency interval $d\ln f = df/f = -d\ln\lambda = -d\lambda/\lambda$. We have with the notations used in (1.4) for spectral densities and integrated fluxes the relations

$$e(f,T) = hfj(f,T) = hf\frac{\partial}{\partial f}j_{[0,f]}(T) = h\frac{\partial}{\partial\ln(f/f_0)}j_{[0,f]}(T)$$
$$= hj(\ln(f/f_0),T) = h\lambda j(\lambda,T) = hj(\ln(\lambda/\lambda_0),T).$$

Optimization of the energy flux of a light source for given frequency bandwidth df is therefore equivalent to optimization of photon flux for fixed fractional bandwidth $df/f = |d\lambda/\lambda|$.

The number of photons per area, per second, and per unit of wavelength emitted from a heat source of temperature T is

$$j(\lambda,T) = \frac{\lambda}{hc}e(\lambda,T) = \frac{2\pi c}{\lambda^4}\frac{1}{\exp\left(\frac{hc}{\lambda k_BT}\right)-1}.$$

This satisfies

$$\frac{\partial}{\partial\lambda}j(\lambda,T) = \frac{j(\lambda,T)}{\lambda}\left(x\frac{\exp(x)}{\exp(x)-1}-4\right) = 0$$

if

$$\exp(x) = \frac{4}{4-x}.$$

This has the solution $x \simeq 3.921$. The wavelength of maximal spectral photon flux $j(\lambda, T)$ therefore satisfies

$$\lambda_{\max} \cdot T \simeq \frac{hc}{3.921 k_B} = 3670\,\mu\text{m} \cdot \text{K}.$$

This yields for a heat source of temperature $T = 5780$ K (see Figure 1.4)

$$\lambda_{\max} = 635\,\text{nm}, \quad \frac{c}{\lambda_{\max}} = 472\,\text{THz}.$$

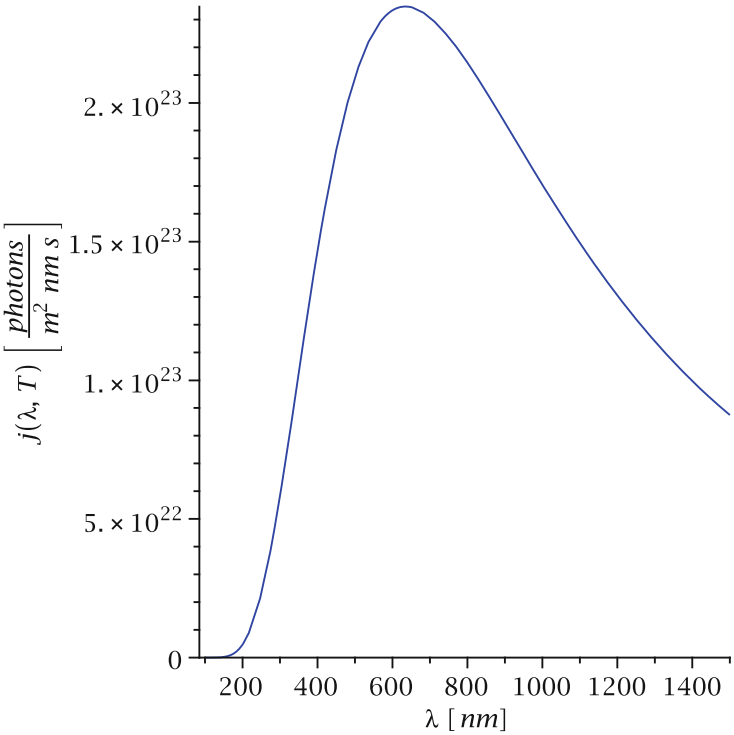


Figure 1.4: The spectral photon flux $j(\lambda, T)$ for a heat source of temperature $T = 5780$ K.

The photon flux in the wavelength scale, $j(\lambda, T)$, is also related to the energy fluxes per fractional wavelength or frequency interval $d \ln \lambda = d\lambda/\lambda = -d \ln f = -df/f$,

$$j(\lambda, T) = \frac{\lambda}{hc} e(\lambda, T) = \frac{1}{hc} e(\ln(\lambda/\lambda_0), T) = \frac{f}{hc} e(f, T) = \frac{1}{hc} e(\ln(f/f_0), T).$$

Therefore optimization of photon flux for fixed wavelength bandwidth $d\lambda$ is equivalent to optimization of energy flux for fixed fractional bandwidth $d\lambda/\lambda = |df/f|$.

Finally, the number of photons per area, per second, and per unit of frequency emitted from a heat source of temperature T is

$$j(f,T) = \frac{e(f,T)}{hf} = \frac{2\pi f^2}{c^2} \frac{1}{\exp\left(\frac{hf}{k_B T}\right) - 1}.$$

This satisfies

$$\frac{\partial}{\partial f} j(f,T) = \frac{j(f,T)}{f} \left(2 - x \frac{\exp(x)}{\exp(x) - 1}\right) = 0$$

if

$$\exp(x) = \frac{2}{2 - x}.$$

This condition is solved by $x \simeq 1.594$. Therefore the frequency of maximal spectral photon flux $j(f,T)$ in the frequency scale satisfies

$$\frac{f_{\max}}{T} \simeq 1.594 \frac{k_B}{h} = 33.21 \, \frac{\mathrm{GHz}}{\mathrm{K}}.$$

This yields for a heat source of temperature $T = 5780$ K (see Figure 1.5)

$$f_{\max} = 192 \, \mathrm{THz}, \quad \frac{c}{f_{\max}} = 1.56 \, \mu\mathrm{m}.$$

The flux of emitted photons is

$$j(T) = \int_0^\infty df \, j(f,T) = 2\pi \frac{k_B^3 T^3}{h^3 c^2} \int_0^\infty dx \, \frac{x^2}{\exp(x) - 1}.$$

Evaluation of the integral

$$\begin{aligned} \int_0^\infty dx \, \frac{x^2}{\exp(x) - 1} &= \int_0^\infty dx \, x^2 \sum_{n=0}^\infty \exp[-(n+1)x] \\ &= \sum_{n=1}^\infty \frac{d^2}{dn^2} \int_0^\infty dx \, \exp(-nx) = \sum_{n=1}^\infty \frac{d^2}{dn^2} \frac{1}{n} \\ &= \sum_{n=1}^\infty \frac{2}{n^3} = 2\zeta(3) \end{aligned}$$

yields

$$j(T) = \frac{4\pi\zeta(3) k_B^3}{h^3 c^2} T^3 = 1.5205 \times 10^{15} \frac{T^3}{\mathrm{m}^2 \cdot \mathrm{s} \cdot \mathrm{K}^3}.$$

A surface temperature $T = 5780$ K for our sun yields a photon flux at the solar surface $2.94 \times 10^{26} \, \mathrm{m}^{-2}\mathrm{s}^{-1}$ and a resulting photon flux at Earth's orbit of $6.35 \times 10^{21} \, \mathrm{m}^{-2}\mathrm{s}^{-1}$. The average photon energy $e(T)/j(T) = 1.35 \, \mathrm{eV}$ is in the infrared.

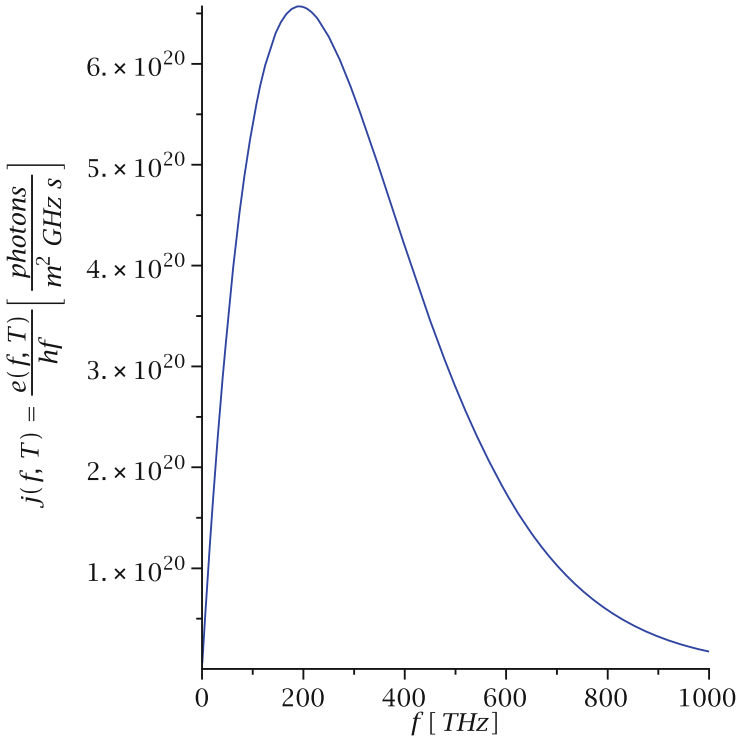


Figure 1.5: The spectral photon flux $j(f,T)$ for a heat source of temperature $T = 5780$ K.

1.4 The photoelectric effect

The notion of energy quanta in radiation was so revolutionary in 1900 that Planck himself speculated that this must somehow be related to the emission mechanism of radiation from the material of the source. In 1905 Albert Einstein pointed out that hitherto unexplained properties of the photoelectric effect can also be explained through energy quanta hf in ultraviolet light, and proposed that this energy quantization is likely an intrinsic property of electromagnetic waves irrespective of how they are generated. In short, the photoelectric effect observations by J.J. Thomson and Lenard revealed the following key properties:

• An ultraviolet light source of frequency f will generate photoelectrons of maximal kinetic energy $hf - hf_0$ if $f > f_0$, where $hf_0 = \phi$ is the minimal energy to liberate photoelectrons from the photocathode.

• Increasing the intensity of the incident ultraviolet light without changing its frequency will increase the photocurrent, but not change the maximal kinetic energy of the photoelectrons. Increasing the intensity must therefore liberate

more photoelectrons from the photocathode, but does not impart more energy on single electrons.
Einstein realized that this behavior can be explained if the incident ultraviolet light of frequency f comes in energy parcels of magnitude hf, and if the electrons in the metal can (predominantly) only absorb a single of these energy parcels.

1.5 Wave-particle duality

When X-rays of wavelength λ_0 are scattered off atoms, one observes scattered X-rays of the same wavelength λ_0 in all directions. However, in the years 1921-1923 Arthur H. Compton observed that under every scattering angle ϑ against the direction of incidence, there is also a component of scattered X-rays with a longer wavelength

$$\lambda = \lambda_0 + \lambda_C(1 - \cos\vartheta)\,.$$

The constant $\lambda_C = 2.426$ pm has the same value for every atom. Compton (and also Debye) recognized that this longer wavelength component in the scattered radiation can be explained as a consequence of particle like collision of Planck's and Einstein's energy parcels hf with weakly bound electrons, if the energy parcels also carry momentum h/λ. Energy conservation during the collision of the electromagnetics energy parcels (meanwhile called photons) with weakly bound electrons ($\boldsymbol{p}'_e$ is the momentum of the recoiling electron),

$$m_e c + \frac{h}{\lambda_0} = \sqrt{p_e'^2 + m_e^2 c^2} + \frac{h}{\lambda},$$

yields

$$p_e'^2 = \frac{h^2}{\lambda_0^2} + \frac{h^2}{\lambda^2} - 2\frac{h^2}{\lambda\lambda_0} + 2m_e hc\left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right),$$

while momentum conservation implies

$$p_e'^2 = \frac{h^2}{\lambda_0^2} + \frac{h^2}{\lambda^2} - 2\frac{h^2}{\lambda\lambda_0}\cos\vartheta.$$

This yields for the wavelength of the scattered photon

$$\lambda = \lambda_0 + \frac{h}{m_e c}(1 - \cos\vartheta)\,, \tag{1.11}$$

with excellent numerical agreement between $h/m_e c$ and the measured value of λ_C.
From the experimental findings on blackbody radiation, the photoelectric effect, and Compton scattering, and the ideas of Planck, Einstein, and Compton,

an electromagnetic wave of frequency $f = c/\lambda$ appears like a current of particles with energy hf and momentum h/λ. However, electromagnetic waves also show wavelike properties like diffraction and interference. The findings of Planck, Einstein, and Compton combined with the wavelike properties of electromagnetic waves (observed for the first time by Heinrich Hertz) constitute the first observation of *wave-particle duality*. Depending on the experimental setup, a physical system can sometimes behave like a wave and sometimes behave like a particle.

However, the puzzle did not end there. Louis de Broglie recognized in 1923 that the orbits of the old Bohr model could be explained through closed circular electron waves if the electrons are assigned a wavelength $\lambda = h/p$, like photons. Soon thereafter, wavelike behavior of electrons was observed by Clinton Davisson and Lester Germer in 1927, when they observed interference of nonrelativistic electrons scattered off the surface of Nickel crystals. At the same time, George Thomson was sending high energy electron beams (with kinetic energies between 20 keV and 60 keV) through thin metal foils and observed interference of the transmitted electrons, thus also confirming the wave nature of electrons. We can therefore also conclude that *another major motivation for the development of quantum mechanics was to explain wave-particle duality.*

1.6 Why Schrödinger's equation?

The foundations of quantum mechanics were developed between 1900 and 1950 by some of the greatest minds of the 20th century, from Max Planck and Albert Einstein to Richard Feynman and Freeman Dyson. The inner circle of geniuses who brought the nascent theory to maturity were Heisenberg, Born, Jordan, Schrödinger, Pauli, Dirac, and Wigner. Among all the outstanding contributions of these scientists, Schrödinger's invention of his wave equation (1.2) was likely the most important *single step* in the development of quantum mechanics. Understanding this step, albeit in a simplified pedagogical way, is important for learning and understanding quantum mechanics.

Ultimately, basic equations in physics have to prove themselves in comparison with experiments, and the Schrödinger equation was extremely successful in that regard. However, this does not explain how to come up with such an equation. Basic equations in physics cannot be derived from any rigorous theoretical or mathematical framewok. There is no algorithm which could have told Newton to come up with Newton's equation, or would have told Schrödinger how to come up with his equation (or could tell us how to come up with a fundamental theory of quantum gravity). Basic equations in physics have to be invented in an act of creative ingenuity, which certainly requires a lot of brainstorming and diligent review of pertinent experimental facts and solutions of related problems (where known).

It is much easier to accept an equation and start to explore its consequences if the equation makes intuitive sense - if we can start our discussion of Schrö-

dinger's equation with the premise "yes, the hypothesis that Schrödinger's equation solves the problems of energy quantization and wave-particle duality seems intuitively promising and is worth pursuing".
Therefore I will point out how Schrödinger *could* have invented the Schrödinger equation (although his actual thought process was much more involved and was motivated by the connection of the quantization rules of old quantum mechanics with the Hamilton-Jacobi equation of classical mechanics [37]).
The problem is to come up with an equation for the motion of particles, which explains both quantization of energy levels and wave-particle duality.
As a starting point, we recall that the motion of a non-relativistic particle under the influence of a conservative force $\boldsymbol{F}(\boldsymbol{x}) = -\boldsymbol{\nabla} V(\boldsymbol{x})$ is classically described by Newton's equation

$$m\frac{d^2\boldsymbol{x}(t)}{dt^2} = -\boldsymbol{\nabla} V(\boldsymbol{x}(t)),$$

and this equation also implies energy conservation,

$$E = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{x}). \tag{1.12}$$

However, this cannot be the whole story, because Davisson and Germer, and G.P. Thomson had shown that at least electrons sometimes also behave like waves with wavelength $\lambda = h/p$, as predicted by de Broglie. Furthermore, Compton has demonstrated that photons of energy $E = hf$ satisfy the relation $\lambda = h/p$ between wavelength and momentum. This motivates the hypothesis that a non-relativistic particle might also satisfy the relation $E = hf$. A monochromatic plane wave of frequency f, wavelength λ, and direction of motion $\hat{\boldsymbol{k}}$ can be described by a wave function

$$\psi(\boldsymbol{x}, t) = A \exp\left[2\pi \mathrm{i}\left(\frac{\hat{\boldsymbol{k}} \cdot \boldsymbol{x}}{\lambda} - ft\right)\right].$$

Substitution of the relations

$$\lambda = \frac{h}{p}, \quad E = hf = \frac{\boldsymbol{p}^2}{2m}$$

yields with $\hbar \equiv h/2\pi$

$$\psi(\boldsymbol{x}, t) = A \exp\left[\mathrm{i}\left(\frac{\boldsymbol{p} \cdot \boldsymbol{x}}{\hbar} - \frac{\boldsymbol{p}^2}{2m\hbar}t\right)\right].$$

Under the supposition of wave-particle duality, we have to assume that this wave function must somehow be related to the wave properties of free particles as observed in the electron diffraction experiments. However, this wave function satisfies a differential equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{x}, t) = E\psi(\boldsymbol{x}, t) = \frac{\boldsymbol{p}^2}{2m}\psi(\boldsymbol{x}, t) = -\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{x}, t), \tag{1.13}$$

because under the assumption of wave-particle duality we had to replace f with E/h in the exponent, and we used $E = \boldsymbol{p}^2/2m$ for a free particle.
This does not yet tell us how to calculate the wave function which would describe motion of particles in a potential $V(\boldsymbol{x})$. However, comparison of the differential equation (1.13) with the classical energy equation (1.12) can give us the idea to try

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{x},t) = -\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{x},t) + V(\boldsymbol{x})\psi(\boldsymbol{x},t) \tag{1.14}$$

as a starting point for the calculation of wave functions for particles moving in a potential $V(\boldsymbol{x})$. Schrödinger actually found this equation after he had found the time-independent Schrödinger equation (3.3) below, and he had demonstrated that these equations yield the correct spectrum for hydrogen atoms, where

$$V(\boldsymbol{x}) = -\frac{e^2}{4\pi\epsilon_0|\boldsymbol{x}|}.$$

Schrödinger's solution of the hydrogen atom will be discussed in Chapter 7.

1.7 Interpretation of Schrödinger's wave function

The Schrödinger equation was a spectacular success right from the start, but it was not immediately clear what the physical meaning of the complex wave function $\psi(\boldsymbol{x},t)$ is. A natural first guess would be to assume that $|\psi(\boldsymbol{x},t)|^2$ corresponds to a physical density of the particle described by the wave function $\psi(\boldsymbol{x},t)$. In this interpretation, an electron in a quantum state $\psi(\boldsymbol{x},t)$ would have a spatial mass density $m\,|\psi(\boldsymbol{x},t)|^2$ and a charge density $-e\,|\psi(\boldsymbol{x},t)|^2$. This interpretation would imply that waves would have prevailed over particles in wave-particle duality.
However, quantum leaps are difficult to reconcile with a physical density interpretation for $|\psi(\boldsymbol{x},t)|^2$, and Schrödinger, Bohr, Born and Heisenberg developed a statistical interpretation of the wave function which is still the leading paradigm for quantum mechanics. Already in June 1926, the view began to emerge that the wave function $\psi(\boldsymbol{x},t)$ should be interpreted as a probability density amplitude[2] in the sense that

$$P_V(t) = \int_V d^3\boldsymbol{x}\ |\psi(\boldsymbol{x},t)|^2 \tag{1.15}$$

[2]E. Schrödinger, Annalen Phys. 386, 109 (1926), paragraph on pp. 134-135, sentences 2-4: "$\psi\overline{\psi}$ is a kind of *weight function* in the configuration space of the system. The *wave mechanical* configuration of the system is a *superposition* of many, strictly speaking of *all*, kinematically possible point mechanical configurations. Thereby each point mechanical configuration contributes with a certain *weight* to the true wave mechanical configuration, where the weight is just given by $\psi\overline{\psi}$." Of course, a weakness of this early hint at the probability interpretation is the vague reference to a "true wave mechanical configuration". A clearer formulation of this point was offered by Born essentially simultaneously, see the following reference. While there was (and always has been) agreement on the importance of a proba-

is the probability to find a particle (or rather, an excitation of the vacuum with minimal energy mc^2 and certain other quantum numbers) in the volume V at time t. The expectation value for the location of the particle at time t is then

$$\langle \boldsymbol{x} \rangle(t) = \int d^3\boldsymbol{x}\, \boldsymbol{x}\, |\psi(\boldsymbol{x},t)|^2, \tag{1.16}$$

where integrals without explicit limits are taken over the full range of the integration variable, i.e. here over all of $\mathbb{R}^3$. Many individual particle measurements will yield the location $\boldsymbol{x}$ with a frequency proportionally to $|\psi(\boldsymbol{x},t)|^2$, and averaging over the observations will yield the expectation value (1.16) with a variance e.g. for the x coordinate

$$\begin{aligned}\Delta x^2(t) &= \langle (x - \langle x \rangle)^2 \rangle(t) = \langle x^2 \rangle(t) - \langle x \rangle^2(t) \\ &= \int d^3\boldsymbol{x}\, x^2\, |\psi(\boldsymbol{x},t)|^2 - \left(\int d^3\boldsymbol{x}\, x\, |\psi(\boldsymbol{x},t)|^2 \right)^2 .\end{aligned}$$

This interpretation of the relation between the wave function and particle properties was essentially proposed by Max Born in an early paper on quantum mechanical scattering[3].

The Schrödinger equation (1.2) implies a local conservation law for probability

$$\frac{\partial}{\partial t} |\psi(\boldsymbol{x},t)|^2 + \boldsymbol{\nabla} \cdot \boldsymbol{j}(\boldsymbol{x},t) = 0 \tag{1.17}$$

with the probability current density

$$\boldsymbol{j}(\boldsymbol{x},t) = \frac{\hbar}{2im} \Big(\psi^+(\boldsymbol{x},t) \cdot \boldsymbol{\nabla} \psi(\boldsymbol{x},t) - \boldsymbol{\nabla} \psi^+(\boldsymbol{x},t) \cdot \psi(\boldsymbol{x},t) \Big). \tag{1.18}$$

The conservation law (1.17) is important for consistency of the probability interpretation of Schrödinger theory. We assume that the integral

$$P(t) = \int d^3\boldsymbol{x}\ |\psi(\boldsymbol{x},t)|^2$$

over $\mathbb{R}^3$ converges. *A priori* this should yield a time-dependent function $P(t)$. However, equation (1.17) implies

$$\frac{d}{dt} P(t) = 0, \tag{1.19}$$

bilistic interpretation, the question of the concept which underlies those probabilities was a contentious point between Schrödinger, who at that time may have preferred to advance a de Broglie type pilot wave interpretation, and Bohr and Born and their particle-wave complementarity interpretation. In the end the complementarity picture prevailed: There are fundamental degrees of freedom with certain quantum numbers. These degrees of freedom are quantal excitations of the vacuum, and mathematically they are described by quantum fields. Depending on the way they are probed, they exhibit wavelike or corpuscular properties. Whether or not to denote these degrees of freedom as particles is a matter of convenience and tradition.

[3] M. Born, Z. Phys. 38, 803 (1926).

whence $P(t) \equiv P$ is a positive constant. This allows for rescaling $\psi(\boldsymbol{x}, t) \to \psi(\boldsymbol{x}, t)/\sqrt{P}$ such that the new wave function still satisfies equation (1.2) and yields a normalized integral

$$\int d^3\boldsymbol{x}\ |\psi(\boldsymbol{x}, t)|^2 = 1. \tag{1.20}$$

This means that the probability to find the particle anywhere at time t is 1, as it should be. The equations (1.15) and (1.16) make only sense in conjunction with the normalization condition (1.20)
We can also substitute the Schrödinger equation or the local conservation law (1.17) into

$$\langle \boldsymbol{p} \rangle(t) = m\frac{d}{dt}\langle \boldsymbol{x} \rangle(t) = m\int d^3\boldsymbol{x}\ \boldsymbol{x}\frac{\partial}{\partial t}\,|\psi(\boldsymbol{x}, t)|^2 \tag{1.21}$$

to find

$$\langle \boldsymbol{p} \rangle(t) = \int d^3\boldsymbol{x}\ \psi^+(\boldsymbol{x}, t)\frac{\hbar}{\mathrm{i}}\boldsymbol{\nabla}\psi(\boldsymbol{x}, t). \tag{1.22}$$

Equations (1.16) and (1.22) tell us how to extract particle like properties from the wave function $\psi(\boldsymbol{x}, t)$. At first sight, equation (1.22) does not seem to make a lot of intuitive sense. Why should the momentum of a particle be related to the gradient of its wave function? However, recall the Compton-de Broglie relation $p = h/\lambda$. Wave packets which are composed of shorter wavelength components oscillate more rapidly as a function of $\boldsymbol{x}$, and therefore have a larger average gradient. Equation (1.22) is therefore in agreement with a basic relation of wave-particle duality.
A related argument in favor of equation (1.22) arises from substitution of the Fourier transforms[4]

$$\psi(\boldsymbol{x}, t) = \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\ \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\psi(\boldsymbol{k}, t),$$

$$\psi^+(\boldsymbol{x}, t) = \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\ \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\psi^+(\boldsymbol{k}, t)$$

in equations (1.20) and (1.22). This yields

$$\int d^3\boldsymbol{k}\ |\psi(\boldsymbol{k}, t)|^2 = 1$$

and

$$\langle \boldsymbol{p} \rangle(t) = \int d^3\boldsymbol{k}\,\hbar\boldsymbol{k}\,|\psi(\boldsymbol{k}, t)|^2\,,$$

[4]Fourier transformation is reviewed in Section 2.1.

in perfect agreement with the Compton-de Broglie relation $\boldsymbol{p} = \hbar\boldsymbol{k}$. Apparently $|\psi(\boldsymbol{k},t)|^2$ is a probability density in $\boldsymbol{k}$ space in the sense that

$$P_{\tilde{V}}(t) = \int_{\tilde{V}} d^3\boldsymbol{k}\ |\psi(\boldsymbol{k},t)|^2$$

is the probability to find the particle with a wave vector $\boldsymbol{k}$ contained in a volume $\tilde{V}$ in $\boldsymbol{k}$ space.
We can also identify an expression for the energy of a particle which is described by a wave function $\psi(\boldsymbol{x},t)$. The Schrödinger equation (1.2) implies the conservation law

$$\frac{d}{dt}\int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x},t)\left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right)\psi(\boldsymbol{x},t) = 0. \tag{1.23}$$

Here it plays a role that we assumed time-independent potential[5]. In classical mechanics, the conservation law which appears for motion in a time-independent potential is energy conservation. Therefore, we expect that the expectation value for energy is given by

$$\langle E\rangle = \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x},t)\left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right)\psi(\boldsymbol{x},t). \tag{1.24}$$

We will also rederive this at a more advanced level in Chapter 17. From the classical relation (1.12) between energy and momentum of a particle, we should also have

$$\langle E\rangle = \frac{\langle \boldsymbol{p}^2\rangle}{2m} + \langle V(\boldsymbol{x})\rangle. \tag{1.25}$$

Comparison of equations (1.22) and (1.24) yields

$$\langle \boldsymbol{p}^2\rangle(t) = \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x},t)(-\mathrm{i}\hbar\boldsymbol{\nabla})^2\psi(\boldsymbol{x},t),$$

such that calculation of expectation values of powers of momentum apparently amounts to corresponding powers of the differential operator $-\mathrm{i}\hbar\boldsymbol{\nabla}$ acting on the wave function $\psi(\boldsymbol{x},t)$.
Maybe one of the most direct observational confirmations of the statistical interpretation of the wave function was the observation of single particle interference by Tonomura, Endo, Matsuda and Kawasaski[6] in 1988. Electrons are passing through a double slit with a time difference that makes it extremely unlikely that two electrons interfere during their passages through the slit. Behind the slit the electrons are observed with a scintillation screen or a camera. Each individual electron is observed to generate only a single dot on the screen.

[5] Examples of the Schrödinger equation with time-dependent potentials will be discussed in Chapter 13 and following chapters.

[6] A. Tonomura, J. Endo, T. Matsuda, T. Kawasaski, Amer. J. Phys. 57, 117 (1989).

This is the behavior expected from a pointlike particle which is not spread over a physical density distribution. The first few electrons seem to generate a random pattern of dots. However, when more and more electrons hit the screen, their dots generate a collective pattern which exactly corresponds to a distribution $|\psi(\boldsymbol{x},t)|^2$ for double slit interference. This implies that $|\psi(x,y,z_0,t)|^2$ is indeed the probability density for an electron to hit the point $\{x,y\}$ on the screen which is located at z_0, but it is not the physical density of a spatially extended electron[7].
A recent three-slit experiment also confirmed the statistical interpretation of the wave function by proving that the interference patterns from many sequential single particle paths agree with the probability density interpretation of $|\psi(\boldsymbol{x},t)|^2$ for single slit diffraction, double-slit interference, and triple-slit interference[8].

1.8 Problems

1.1 Plot the emittance $e_{[0,\lambda]}(T)$ of our sun.

1.2 Suppose that the resolution of a particular monochromator scales with $1/f$, i.e. if the monochromator is set to a particular frequency f the product $fdf = df^2/2$ of frequency and bandwidth is constant. Furthermore, assume that the monochromator is coupled to a device which produces a signal proportional to the energy of the incident radiation. In the limit $df \to 0$, is the signal curve from this apparatus proportional to $e(f,T)$, $e(\lambda,T)$, $j(f,T)$ or $j(\lambda,T)$?

1.3 Suppose that the resolution of a particular monochromator scales with f, i.e. if the monochromator is set to a particlular frequency f the fractional bandwidth df/f is constant. The monochromator is coupled to a device which produces a signal proportional to the energy of the incident radiation. The device is used for observation of a Planck spectrum. For which relation between frequency and temperature does this device yield maximal signal?

1.4 Derive the probability conservation law (1.17) from the Schrödinger equation. Hint: Multiply the Schrödinger equation with $\psi^+(\boldsymbol{x},t)$ and use also the complex conjugate equation.

1.5 We will often deal with quantum mechanics in d spatial dimensions. There are many motivations to go beyond the standard case $d=3$. E.g. $d=0$ is the number of spatial dimensions for an idealized quantum dot, $d=1$ is often used for pedagogical purposes and also for idealized quantum wires or nanowires, and $d=2$ is used for physics on surfaces and interfaces.
We consider a normalized wave function $\psi(\boldsymbol{x},t)$ in d dimensions. What are

[7] It has been argued that Bohmian mechanics can also explain the Tonomura experiment through a pilot wave interpretation of the wave function. However, Bohmian mechanics has other problems. We will briefly return to Bohmian mechanics in Problem 7.15.

[8] U. Sinha, C. Couteau, T. Jennewein, R. Laflamme, G. Weihs, Science 329, 418 (2010).

the SI units of the wave function? What are the SI units of the d-dimensional current density $\boldsymbol{j}$ for the wave function $\psi(\boldsymbol{x}, t)$?

1.6 Derive equation (1.22) from (1.21).

1.7 Show that the Schrödinger equation (1.14) implies the conservation laws

$$\frac{d}{dt}\int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x},t)\left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right)^n \psi(\boldsymbol{x},t) = 0, \quad n \in \mathbb{N}_0. \tag{1.26}$$

Two particular cases of this equation appeared in Section 1.7. Which are those cases and what are the related conserved quantities?
Why is there usually not much interest in the infinitely many higher order conservation laws (1.26) for $n > 1$? Hint: Think about the classical interpretation of these conservation laws.
Why do the higher order conservation laws nevertheless matter in quantum mechanics? Hint: Equation (1.26) is generically different from the "similar" conservation law $d(\langle E\rangle^n)/dt = 0$. Is there an interesting implication of the two conservation laws for $n = 2$?

1.8 Equation (1.21) implies that the equation $\boldsymbol{p}(t) = m d\boldsymbol{x}(t)/dt$ from non-relativistic classical mechanics is realized as an equation between expectation values in non-relativistic quantum mechanics. Show that Newton's law holds in the following sense in non-relativistic quantum mechanics (Ehrenfest's theorem),

$$\frac{d}{dt}\langle \boldsymbol{p}\rangle(t) = -\langle \boldsymbol{\nabla} V(\boldsymbol{x})\rangle(t).$$

Chapter 2

Self-adjoint Operators and Eigenfunction Expansions

The relevance of waves in quantum mechanics naturally implies that the decomposition of arbitrary wave packets in terms of monochromatic waves, commonly known as Fourier decomposition after Jean-Baptiste Fourier's *Théorie analytique de la Chaleur* (1822), plays an important role in applications of the theory. Dirac's δ function, on the other hand, gained prominence primarily through its use in quantum mechanics, although today it is also commonly used in mechanics and electrodynamics to describe sudden impulses, mass points, or point charges. Both concepts are intimately connected to the completeness of eigenfunctions of self-adjoint operators. From the quantum mechanics perspective, the problem of completeness of sets of functions concerns the problem of enumeration of all possibe states of a quantum system.

2.1 The δ function and Fourier transforms

Let $f(x)$ be a smooth function in the interval $[a, b]$. Dirichlet's equation [6]

$$\lim_{\kappa\to\infty}\int_a^b dx'\,\frac{\sin(\kappa(x-x'))}{\pi(x-x')}f(x') = \begin{cases} 0, & x\notin[a,b],\\ f(x), & x\in(a,b),\end{cases} \tag{2.1}$$

motivates the formal definition

$$\begin{aligned}\delta(x) &= \lim_{\kappa\to\infty}\frac{\sin(\kappa x)}{\pi x} = \lim_{\kappa\to\infty}\frac{1}{2\pi}\int_{-\kappa}^{\kappa} dk\,\exp(\mathrm{i}kx)\\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dk\,\exp(\mathrm{i}kx),\end{aligned} \tag{2.2}$$

such that equation (2.1) can (in)formally be written as

$$\int_a^b dx'\,\delta(x-x')f(x') = \begin{cases} 0, & x\notin[a,b],\\ f(x), & x\in(a,b).\end{cases}$$

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A justification for Dirichlet's equation is given below in the derivation of equation (2.7).
The generalization to three dimensions follows immediately from Dirichlet's formula in a three-dimensional cube, and exhaustion of an arbitrary three-dimensional volume V by increasingly finer cubes. This yields

$$\delta(\boldsymbol{x}) = \lim_{|\boldsymbol{\kappa}|\to\infty} \prod_{i=1}^{3} \frac{\sin(\kappa_i x_i)}{\pi x_i} = \frac{1}{(2\pi)^3} \int d^3\boldsymbol{k}\, \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}), \tag{2.3}$$

$$\int_V d^3\boldsymbol{x}'\, \delta(\boldsymbol{x}-\boldsymbol{x}') f(\boldsymbol{x}') = \begin{cases} 0, & \boldsymbol{x} \notin V, \\ f(\boldsymbol{x}), & \boldsymbol{x} \text{ inside } V. \end{cases}$$

The case $\boldsymbol{x} \in \partial V$ ($\boldsymbol{x}$ on the boundary of V) must be analyzed on a case-by-case basis.
Equation (2.3) implies

$$\begin{aligned} \psi(\boldsymbol{x},t) &= \int d^3\boldsymbol{x}'\, \delta(\boldsymbol{x}-\boldsymbol{x}')\psi(\boldsymbol{x}',t) \\ &= \frac{1}{(2\pi)^3} \int d^3\boldsymbol{k}\, \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \int d^3\boldsymbol{x}'\, \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}')\psi(\boldsymbol{x}',t). \end{aligned}$$

This can be used to introduce Fourier transforms by splitting the previous equation into two equations,

$$\psi(\boldsymbol{x},t) = \frac{1}{\sqrt{2\pi}^3} \int d^3\boldsymbol{k}\, \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\psi(\boldsymbol{k},t), \tag{2.4}$$

with

$$\psi(\boldsymbol{k},t) = \frac{1}{\sqrt{2\pi}^3} \int d^3\boldsymbol{x}\, \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\psi(\boldsymbol{x},t). \tag{2.5}$$

Use of $\psi(\boldsymbol{x},t)$ corresponds to the $\boldsymbol{x}$-*representation* of quantum mechanics. Use of $\psi(\boldsymbol{k},t)$ corresponds to the $\boldsymbol{k}$-*representation* or *momentum-representation* of quantum mechanics.
The notation above for Fourier transforms is a little sloppy, but convenient and common in quantum mechanics. From a mathematical perspective, the Fourier transformed function $\psi(\boldsymbol{k},t)$ should actually be denoted by $\tilde{\psi}(\boldsymbol{k},t)$ to make it clear that it is *not* the same function as $\psi(\boldsymbol{x},t)$ with different symbols for the first three variables. The physics notation is motivated by the observation that $\psi(\boldsymbol{x},t)$ and $\psi(\boldsymbol{k},t)$ are just different representations of the same quantum mechanical state ψ.
Another often used convention for Fourier transforms is to split the factor $(2\pi)^{-3}$ asymmetrically, or equivalently replace it with a factor 2π in the exponents,

$$\psi(\boldsymbol{x},t) = \frac{1}{(2\pi)^3} \int d^3\boldsymbol{k}\, \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\psi(\boldsymbol{k},t),$$

$$\psi(\boldsymbol{k},t) = \int d^3\boldsymbol{x}\, \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\psi(\boldsymbol{x},t),$$

or equivalently

$$\psi(\boldsymbol{x},t) = \int d^3\tilde{\boldsymbol{\nu}}\, \exp(2\pi\mathrm{i}\tilde{\boldsymbol{\nu}}\cdot\boldsymbol{x})\psi(\tilde{\boldsymbol{\nu}},t),$$

$$\psi(\tilde{\boldsymbol{\nu}},t) = \int d^3\boldsymbol{x}\, \exp(-2\pi\mathrm{i}\tilde{\boldsymbol{\nu}}\cdot\boldsymbol{x})\psi(\boldsymbol{x},t),$$

with the vector of wavenumbers

$$\tilde{\boldsymbol{\nu}} = \frac{\boldsymbol{k}}{2\pi}.$$

The conventions (2.4, 2.5) are used throughout this book.
The following is an argument for equation (2.1) and its generalizations to other representations of the δ function. The idea is to first construct a limit for the Heaviside step function or Θ function

$$\Theta(x) = \begin{cases} 1, & x > 0, \\ 0, & x < 0, \end{cases}$$

and go from there. The value of $\Theta(0)$ is often chosen to suite the needs of the problem at hands. The choice $\Theta(0) = 1/2$ seems intuitive and is also mathematically natural in the sense that any decomposition of a discontinuous functions in a complete set of functions (e.g. Fourier decomposition) will approximate the mean value between the left and right limit for a finite discontinuity, but in many applications other values of $\Theta(0)$ are preferred.
The Θ function helps us to explain Dirichlet's equation (2.1) through the following construction. Suppose $d(x)$ is a normalized function,

$$\int_{-\infty}^{\infty} dx\, d(x) = 1. \tag{2.6}$$

The integral

$$D(x) = \int_{-\infty}^{x} d\xi\, d(\xi)$$

satisfies

$$\lim_{\kappa\to\infty} D(\kappa\cdot x) = \Theta(x), \tag{2.7}$$

where we apparently defined $\Theta(0)$ as $\Theta(0) = \int_{-\infty}^{0} d\xi\, d(\xi)$, but this plays no role for the following reasoning.
Equation (2.7) yields for $f(x)$ differentiable in $[a,b]$

$$\int_a^b dx\, \kappa\, d(\kappa\cdot x) f(x) = D(\kappa\cdot x) f(x)\Big|_a^b - \int_a^b dx\, D(\kappa\cdot x) f'(x),$$

$$\begin{aligned}\lim_{\kappa\to\infty}\int_a^b dx\,\kappa\,d(\kappa\cdot x)f(x) &= \Theta(b)f(b)-\Theta(a)f(a)-\int_0^b dx\,\Theta(x)f'(x)\\ &\quad+\int_0^a dx\,\Theta(x)f'(x)\\ &= \Theta(b)f(b)-\Theta(a)f(a)-\Theta(b)[f(b)-f(0)]\\ &\quad+\Theta(a)[f(a)-f(0)]\\ &= [\Theta(b)-\Theta(a)]f(0), \end{aligned} \tag{2.8}$$

and therefore

$$\lim_{\kappa\to\infty}\kappa\,d(\kappa x)=\delta(x), \tag{2.9}$$

or after shifting the argument,

$$\lim_{\kappa\to\infty}\kappa\,d[\kappa(x-x_0)]=\delta(x-x_0).$$

From a mathematical perspective, equations like (2.9) mean that the action of the δ distribution on a smooth funtion corresponds to integration with a kernel $\kappa\,d(\kappa x)$ and then taking the limit $\kappa\to\infty$.
Equation (2.2) is an important particular realization of equation (2.9) with $d(x)=\sin(x)/\pi x$. Another important realization uses the function $d(x)=(\pi+\pi x^2)^{-1}$,

$$\begin{aligned}\delta(x) &= \lim_{\kappa\to\infty}\frac{1}{\pi}\frac{\kappa}{1+\kappa^2x^2}=\lim_{a\to0}\frac{1}{\pi}\frac{a}{a^2+x^2}\\ &= \lim_{a\to0}\frac{1}{2\pi}\int_{-\infty}^{\infty}dk\,\exp(\mathrm{i}kx-a|k|). \end{aligned} \tag{2.10}$$

Note that we did not require $d(x)$ to have a maximum at $x=0$ to derive (2.9), and indeed we do not need this requirement. Consider the following example,

$$d(x)=\frac{1}{2}\sqrt{\frac{\alpha}{\pi}}\exp[-\alpha(x-a)^2]+\frac{1}{2}\sqrt{\frac{\beta}{\pi}}\exp[-\beta(x-b)^2].$$

This function has two maxima if $\alpha\cdot\beta\neq0$ and if a and b are sufficiently far apart, and it even has a minimum at $x=0$ if $\alpha=\beta$ and $a=-b$. Yet we still have

$$\begin{aligned}\lim_{\kappa\to\infty}\kappa\,d(\kappa\cdot x) = \lim_{\kappa\to\infty}\Bigg(&\frac{\kappa}{2}\sqrt{\frac{\alpha}{\pi}}\exp[-\alpha(\kappa x-a)^2]\\ &+\frac{\kappa}{2}\sqrt{\frac{\beta}{\pi}}\exp[-\beta(\kappa x-b)^2]\Bigg)=\delta(x),\end{aligned}$$

because the scaling with κ scales the initial maxima near a and b to $a/\kappa\to0$ and $b/\kappa\to0$.

Sokhotsky-Plemelj relations

The Sokhotsky-Plemelj relations are very useful relations involving a δ distribution[1],

$$\frac{1}{x-\mathrm{i}\epsilon} = \mathcal{P}\frac{1}{x} + \mathrm{i}\pi\delta(x), \quad \frac{1}{x+\mathrm{i}\epsilon} = \mathcal{P}\frac{1}{x} - \mathrm{i}\pi\delta(x). \tag{2.11}$$

Indeed, for the practical evaluation of integrals involving singular denominators, we virtually never use these relations but evaluate the integrals with the left hand sides directly using the Cauchy and residue theorems. The primary use of the Sokhotsky-Plemelj relations in physics and technology is to establish relations between different physical quantities. The relation between retarded Green's functions and local densities of states is an example for this and will be derived in Section 20.1.

I will give a brief justification for the Sokhotsky-Plemelj relations. The relations

$$\frac{1}{x+\mathrm{i}\epsilon} = \frac{1}{\mathrm{i}}\int_0^\infty dk\, \exp[\mathrm{i}k(x+\mathrm{i}\epsilon)] = \frac{1}{\mathrm{i}}\int_{-\infty}^0 dk\, \exp[-\mathrm{i}k(x+\mathrm{i}\epsilon)]$$

imply

$$\Im\frac{1}{x+\mathrm{i}\epsilon} = -\frac{1}{2}\int_{-\infty}^\infty dk\, \cos(kx) = -\pi\delta(x).$$

On the other hand, the real part is

$$\Re\frac{1}{x+\mathrm{i}\epsilon} = \frac{1}{2(x+\mathrm{i}\epsilon)} + \frac{1}{2(x-\mathrm{i}\epsilon)} = \frac{x}{x^2+\epsilon^2}.$$

This implies for integration with a bounded function $f(x)$ in $[a,b]$

$$\int_a^b dx\, \frac{f(x)}{x+\mathrm{i}\epsilon} = \int_a^b dx\, \frac{xf(x)}{x^2+\epsilon^2} - \mathrm{i}\pi[\Theta(b)-\Theta(a)]f(0).$$

However, the weight factor

$$K_\epsilon(x) = \frac{x}{x^2+\epsilon^2}$$

esentially cuts the region $-3\epsilon < x < 3\epsilon$ symmetrically from the integral $\int_a^b dx\, f(x)/x$ (the value 3ϵ is chosen because $xK_\epsilon(x) = 0.9$ for $x = \pm 3\epsilon$), see Fig. 2.1. Therefore we can use this factor as one possible definition of a principal value integral,

$$\mathcal{P}\int_a^b dx\, \frac{f(x)}{x} = \lim_{\epsilon\to 0}\int_a^b dx\, K_\epsilon(x) f(x).$$

[1] Yu.V. Sokhotsky, Ph.D. thesis, University of St. Petersburg, 1873; J. Plemelj, Monatshefte Math. Phys. 19, 205 (1908). The "physics" version (2.11) of the Sokhotsky-Plemelj relations is of course more recent than the original references because the δ distribution was only introduced much later.

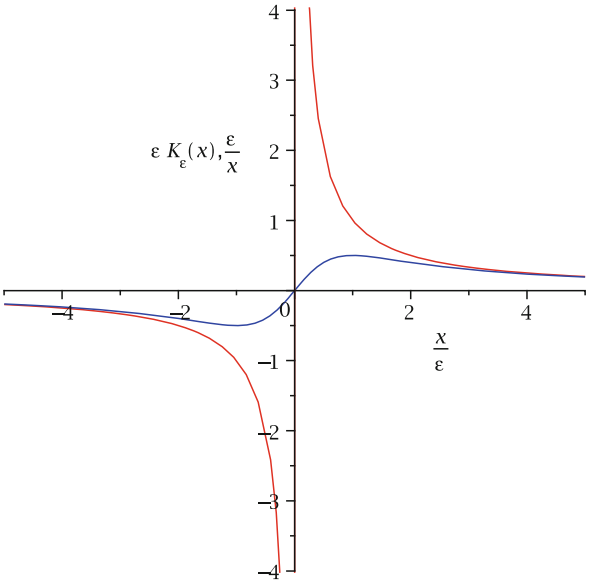


Figure 2.1: Comparison of $1/x$ with the weight factor $K_\epsilon(x)$.

2.2 Self-adjoint operators and completeness of eigenstates

The statistical interpretation of the wave function $\psi(\boldsymbol{x}, t)$ implies that the wave functions of single stable particles should be normalized,

$$\int d^3\boldsymbol{x}\, |\psi(\boldsymbol{x}, t)|^2 = 1. \tag{2.12}$$

Time-dependence plays no role and will be suppressed in the following investigations.
Indeed, we have to require a little more than just normalizability of the wave function $\psi(\boldsymbol{x})$ itself, because the functions $\boldsymbol{\nabla}\psi(\boldsymbol{x})$, $\Delta\psi(\boldsymbol{x})$, and $V(\boldsymbol{x})\psi(\boldsymbol{x})$ for admissible potentials $V(\boldsymbol{x})$ should also be square integrable. We will therefore also encounter functions $f(\boldsymbol{x})$ which may not be normalized, although they are square integrable,

$$\int d^3\boldsymbol{x}\, |f(\boldsymbol{x})|^2 < \infty.$$

Let $\psi(\boldsymbol{x})$ and $\phi(\boldsymbol{x})$ be two square integrable functions. The identity

$$\int d^3\boldsymbol{x}\, |\psi(\boldsymbol{x}) - \lambda\phi(\boldsymbol{x})|^2 \geq 0$$

yields with the choice

$$\lambda = \frac{\int d^3\boldsymbol{x}\, \phi^+(\boldsymbol{x})\psi(\boldsymbol{x})}{\int d^3\boldsymbol{x}\, |\phi(\boldsymbol{x})|^2}$$

the Schwarz inequality

$$\left| \int d^3\boldsymbol{x}\, \phi^+(\boldsymbol{x})\psi(\boldsymbol{x}) \right|^2 \leq \int d^3\boldsymbol{x}\, |\psi(\boldsymbol{x})|^2 \int d^3\boldsymbol{x}'\, |\phi(\boldsymbol{x}')|^2.$$

The differential operators $-\mathrm{i}\hbar\boldsymbol{\nabla}$ and $-(\hbar^2/2m)\Delta$, which we associated with momentum and kinetic energy, and the potential energy $V(\boldsymbol{x})$ all have the following properties,

$$\int d^3\boldsymbol{x}\, \phi^+(\boldsymbol{x}) \frac{\hbar}{\mathrm{i}} \boldsymbol{\nabla}\psi(\boldsymbol{x}) = \left(\int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x}) \frac{\hbar}{\mathrm{i}} \boldsymbol{\nabla}\phi(\boldsymbol{x}) \right)^+, \tag{2.13}$$

$$\int d^3\boldsymbol{x}\, \phi^+(\boldsymbol{x}) \Delta\psi(\boldsymbol{x}) = \left(\int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x}) \Delta\phi(\boldsymbol{x}) \right)^+, \tag{2.14}$$

and

$$\int d^3\boldsymbol{x}\, \phi^+(\boldsymbol{x}) V(\boldsymbol{x})\psi(\boldsymbol{x}) = \left(\int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x}) V(\boldsymbol{x})\phi(\boldsymbol{x}) \right)^+. \tag{2.15}$$

Equation (2.15) is a consequence of the fact that $V(\boldsymbol{x})$ is a real function. Equations (2.13, 2.14) are a direct consequence of partial integrations and the fact that boundary terms at $|\boldsymbol{x}| \to \infty$ vanish under the assumptions that we had imposed on the wave functions.
If two operators $A_{\boldsymbol{x}}$ and $B_{\boldsymbol{x}}$ have the property

$$\int d^3\boldsymbol{x}\, \phi^+(\boldsymbol{x}) A_{\boldsymbol{x}}\psi(\boldsymbol{x}) = \left(\int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x}) B_{\boldsymbol{x}}\phi(\boldsymbol{x}) \right)^+, \tag{2.16}$$

for *all* wave functions of interest, then $B_{\boldsymbol{x}}$ is denoted as *adjoint* to the operator $A_{\boldsymbol{x}}$. The mathematical notation for the adjoint operator to $A_{\boldsymbol{x}}$ is $A^+_{\boldsymbol{x}}$,

$$B_{\boldsymbol{x}} = A^+_{\boldsymbol{x}}.$$

Complex conjugation of (2.16) then immediately tells us $B^+_{\boldsymbol{x}} = A_{\boldsymbol{x}}$.
An operator with the property $A^+_{\boldsymbol{x}} = A_{\boldsymbol{x}}$ is denoted as a *self-adjoint* or *hermitian* operator[2]. Self-adjoint operators are important in quantum mechanics

[2]We are not addressing matters of definition of domains of operators in function spaces, see e.g. [19] or problem 4. If the operators $A^+_{\boldsymbol{x}}$ and $A_{\boldsymbol{x}}$ can be defined on different classes of functions, and $A^+_{\boldsymbol{x}} = A_{\boldsymbol{x}}$ holds on the intersections of their domains, then $A_{\boldsymbol{x}}$ is usually denoted as a *symmetric operator*. The notion of self-adjoint operator requires identical domains for both $A_{\boldsymbol{x}}$ and $A^+_{\boldsymbol{x}}$ such that the domain of neither operator can be extended. If the conditions on the domains are violated, we can e.g. have a situation where $A_{\boldsymbol{x}}$ has no eigenfunctions at all, or where the eigenvalues of $A_{\boldsymbol{x}}$ are complex and the set of eigenfunctions is overcomplete. Hermiticity is sometimes defined as equivalent to symmetry or as equivalent to the more restrictive notion of self-adjointness of operators. We define Hermiticity as self-adjointness.

because they yield real expectation values,

$$(\langle A\rangle_\psi)^+ = \left(\int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x})A_{\boldsymbol{x}}\psi(\boldsymbol{x})\right)^+ = \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x})A^+_{\boldsymbol{x}}\psi(\boldsymbol{x})$$
$$= \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x})A_{\boldsymbol{x}}\psi(\boldsymbol{x}) = \langle A\rangle_\psi.$$

Observable quantities like energy or momentum or location of a particle are therefore implemented through self-adjoint operators, e.g. momentum $\boldsymbol{p}$ through the self-adjoint differential operator $-\mathrm{i}\hbar\boldsymbol{\nabla}$.
Self-adjoint operators have the further important property that their eigenfunctions yield *complete sets* of functions. Schematically this means the following: Suppose we can enumerate all constants $a_{\boldsymbol{n}}$ and functions $\psi_{\boldsymbol{n}}(\boldsymbol{x})$ which satisfy the equation

$$A_{\boldsymbol{x}}\psi_{\boldsymbol{n}}(\boldsymbol{x}) = a_{\boldsymbol{n}}\psi_{\boldsymbol{n}}(\boldsymbol{x}) \tag{2.17}$$

with the set of discrete indices $\boldsymbol{n}$. The constants $a_{\boldsymbol{n}}$ are *eigenvalues* and the functions $\psi_{\boldsymbol{n}}(\boldsymbol{x})$ are *eigenfunctions* of the operator $A_{\boldsymbol{x}}$. Hermiticity of the operator $A_{\boldsymbol{x}}$ implies orthogonality of eigenfunctions for different eigenvalues,

$$a_{\boldsymbol{n}}\int d^3\boldsymbol{x}\,\psi^+_{\boldsymbol{m}}(\boldsymbol{x})\psi_{\boldsymbol{n}}(\boldsymbol{x}) = \int d^3\boldsymbol{x}\,\psi^+_{\boldsymbol{m}}(\boldsymbol{x})A_{\boldsymbol{x}}\psi_{\boldsymbol{n}}(\boldsymbol{x})$$
$$= \left(\int d^3\boldsymbol{x}\,\psi^+_{\boldsymbol{n}}(\boldsymbol{x})A_{\boldsymbol{x}}\psi_{\boldsymbol{m}}(\boldsymbol{x})\right)^+$$
$$= a_{\boldsymbol{m}}\int d^3\boldsymbol{x}\,\psi^+_{\boldsymbol{m}}(\boldsymbol{x})\psi_{\boldsymbol{n}}(\boldsymbol{x})$$

and therefore

$$\int d^3\boldsymbol{x}\,\psi^+_{\boldsymbol{m}}(\boldsymbol{x})\psi_{\boldsymbol{n}}(\boldsymbol{x}) = 0 \text{ if } a_{\boldsymbol{n}} \neq a_{\boldsymbol{m}}.$$

However, even if $a_{\boldsymbol{n}} = a_{\boldsymbol{m}}$ for different indices $\boldsymbol{n} \neq \boldsymbol{m}$ (i.e. if the eigenvalue $a_{\boldsymbol{n}}$ is *degenerate* because there exist at least two eigenfunctions with the same eigenvalue), one can always chose orthonormal sets of eigenfunctions for a degenerate eigenvalue. We therefore require

$$\int d^3\boldsymbol{x}\,\psi^+_{\boldsymbol{m}}(\boldsymbol{x})\psi_{\boldsymbol{n}}(\boldsymbol{x}) = \delta_{\boldsymbol{m},\boldsymbol{n}}. \tag{2.18}$$

Completeness of the set of functions $\psi_{\boldsymbol{n}}(\boldsymbol{x})$ means that an "arbitrary" function $f(\boldsymbol{x})$ can be expanded in terms of the eigenfunctions of the self-adjoint operator $A_{\boldsymbol{x}}$ in the form

$$f(\boldsymbol{x}) = \sum_{\boldsymbol{n}} c_{\boldsymbol{n}}\psi_{\boldsymbol{n}}(\boldsymbol{x}) \tag{2.19}$$

with expansion coefficients

$$c_{\boldsymbol{n}} = \int d^3\boldsymbol{x}\,\psi^+_{\boldsymbol{n}}(\boldsymbol{x})f(\boldsymbol{x}). \tag{2.20}$$

If we substitute equation (2.20) into (2.19) and (in)formally exchange integration and summation, we can express the completeness property of the set of functions $\psi_{\boldsymbol{n}}(\boldsymbol{x})$ in the *completeness relation*

$$\sum_{\boldsymbol{n}} \psi_{\boldsymbol{n}}(\boldsymbol{x})\psi^{+}_{\boldsymbol{n}}(\boldsymbol{x}') = \delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{2.21}$$

Both the existence and the meaning of the series expansions (2.19,2.20) depends on what large a class of "arbitrary" functions $f(\boldsymbol{x})$ one considers. Minimal constraints require boundedness of $f(\boldsymbol{x})$, and continuity if the series (2.19) is supposed to converge pointwise. The default constraints in non-relativistic quantum mechanics are continuity of wave functions $\psi(\boldsymbol{x})$ to ensure validity of the Schrödinger equation with at most finite discontinuities in potentials $V(\boldsymbol{x})$, and normalizability. Under these circumstances the expansion (2.19, 2.20) for a wave function $f(\boldsymbol{x}) \equiv \psi(\boldsymbol{x})$ will converge pointwise to $\psi(\boldsymbol{x})$. However, it is convenient for many applications of quantum mechanics to use limiting forms of wave functions which are not normalizable in the sense of equation (2.12) any more, e.g. plane wave states $\psi_{\boldsymbol{k}}(\boldsymbol{x}) \propto \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})$, and we will frequently also have to expand non-continuous functions, e.g. functions of the form $f(\boldsymbol{x}) = V(\boldsymbol{x})\psi(\boldsymbol{x})$ with a discontinuous potential $V(\boldsymbol{x})$. However, finally we only have to use expansions of the form (2.19, 2.20) in the evaluation of integrals of the form $\int d^3\boldsymbol{x} g^{+}(\boldsymbol{x})f(\boldsymbol{x})$, and here the concept of *convergence in the mean* comes to our rescue in the sense that substitution of the series expansion (2.19, 2.20) in the integral will converge to the same value of the integral, even if the expansion (2.19, 2.20) does not converge pointwise to the function $f(\boldsymbol{x})$. A more thorough discussion of completeness of sets of eigenfunctions of self-adjoint operators in the relatively simple setting of wave functions confined to a finite one-dimensional interval is presented in Appendix C. However, for a first reading I would recommend to accept the series expansions (2.19,2.20) with the assurance that substitutions of these series expansions is permissible in the calculation of observables in quantum mechanics.

2.3 Problems

2.1 Suppose the function $f(x)$ has only first order zeros, i.e. we have non-vanishing slope at all nodes x_i of the function,

$$f(x_i) = 0 \;\;\Rightarrow\;\; f'(x_i) \equiv \left.\frac{df(x)}{dx}\right|_{x=x_i} \neq 0.$$

Prove the following property of the δ function:

$$\delta(f(x)) = \sum_i \frac{1}{|f'(x_i)|}\delta(x-x_i).$$

2.2 Calculate the Fourier transforms of the following functions, where in all cases $-\infty < x < \infty$. Do not use any electronic integration program.

2.2a $\psi_1(x) = \exp(-ax^2)$, $\Re a > 0$,
2.2b $\psi_2(x) = 1/(a^2 + x^2)$, $a > 0 \in \mathbb{R}$,
2.2c $\psi_3(x) = x^n \exp(-a|x|)$, $a > 0 \in \mathbb{R}$, where n is a natural number.

2.3 We consider a finite interval $[a, b]$ together with the set $C^{(1,\alpha)}[a, b]$ of complex valued functions which are continuous in $[a, b]$ and differentiable in (a, b), and satisfy the pseudo-periodicity condition

$$\psi(b) = \exp(\mathrm{i}\alpha)\psi(a), \quad \alpha \in \mathbb{R}.$$

Show that the differential operator $-\mathrm{i}d/dx$ is self-adjoint on $C^{(1,\alpha)}[a, b]$. Give a complete set of eigenstates of $-\mathrm{i}d/dx$ in $C^{(1,\alpha)}[a, b]$.

2.4 We consider the finite interval $[a, b]$ together with the set $C^{(2),0}[a, b]$ of complex valued functions which are continuous in $[a, b]$ and second order differentiable in (a, b), and satisfy the boundary conditions

$$\psi(a) = \psi(b) = 0.$$

Show that that the differential operator d^2/dx^2 is self-adjoint on $C^{(2),0}[a, b]$. Give a complete set of eigenstates of d^2/dx^2 in $C^{(2),0}[a, b]$.

2.5 We consider the finite interval $[a, b]$ together with the set $C^{(1),0}[a, b]$ of complex valued functions which are continuous in $[a, b]$ and differentiable in (a, b), and satisfy the boundary conditions

$$\psi(a) = \psi(b) = 0.$$

Show that the symmetric differential operator $h_1 = -\mathrm{i}d/dx$ with domain $C^{(1),0}[a, b]$ is not self-adjoint in the sense that h_1^+ can be defined on the larger set $L_2[a, b]$ of square integrable functions over $[a, b]$.
Show that h_1 has no eigenstates, while h_1^+ has complex eigenvalues and an overcomplete set of eigenstates.

Chapter 3

Simple Model Systems

One-dimensional models and models with piecewise constant potentials have been used as simple model systems for quantum behavior ever since the inception of Schrödinger's equation. These models vary in their levels of sophistication, but their generic strength is the clear demonstration of important general quantum effects and effects of dimensionality of a quantum system at very little expense in terms of effort or computation. Simple model systems are therefore more than just pedagogical tools for teaching quantum mechanics. They also serve as work horses for the modeling of important quantum effects in nanoscience and technology, see e.g. [3, 18].

3.1 Barriers in quantum mechanics

Widely used models for quantum behavior in solid state electronics are described by piecewise constant potentials $V(\boldsymbol{x})$. This means that $V(\boldsymbol{x})$ attains constant values in different regions of space, and the transition between those regions of constant $V(\boldsymbol{x})$ appears through discontinuous jumps in the potential. Figure 3.1 shows an example of a piecewise constant potential.
The Schrödinger equation with a piecewise constant potential is easy to solve, and the solutions provide instructive examples for the impact of quantum effects on the motion of charge carriers through semiconductors and insulating barriers. We will first discuss the case of a rectangular barrier.
Figure 3.1 shows a cross section of a non-symmetric rectangular square barrier. The piecewise constant potential has values

$$V(\boldsymbol{x}) = \begin{cases} 0, & x < 0, \\ \Phi_1, & 0 \leq x \leq L, \\ \Phi_2, & x > L. \end{cases}$$

with $\Phi_1 > \Phi_2 > 0$. This barrier impedes motion in the x direction. It can be used e.g. as a simple quantum mechanical model for a metal coated with an insulating layer. The region $x < 0$ would be inside the metal and the potential Φ_2 would be the energy which is required to liberate an electron from the

R. Dick, *Advanced Quantum Mechanics: Materials and Photons*,
Graduate Texts in Physics, DOI 10.1007/978-1-4419-8077-9_3,
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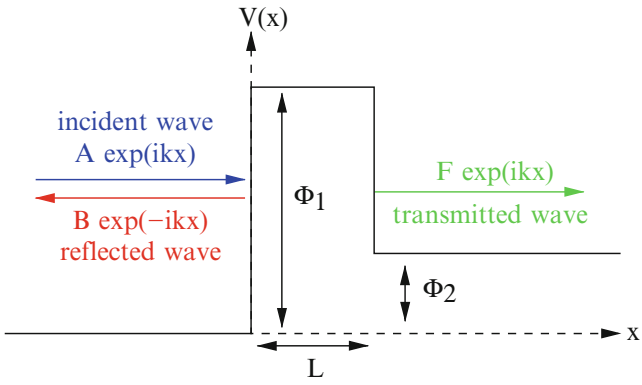


Figure 3.1: A non-symmetric square barrier.

metal if there would not be the insulating layer of thickness L. The energy Φ_1 is the energy which would classically be required for an electron to penetrate the layer.

Quantum problems with time-independent potentials are conveniently analyzed by using a Fourier transformation[1] from time t to energy E,

$$\psi(\boldsymbol{x},t) = \frac{1}{\sqrt{2\pi}\hbar}\int_{-\infty}^{\infty} dE\, \exp\left(-\frac{\mathrm{i}}{\hbar}Et\right)\psi(\boldsymbol{x},E), \tag{3.1}$$

$$\psi(\boldsymbol{x},E) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dt\, \exp\left(\frac{\mathrm{i}}{\hbar}Et\right)\psi(\boldsymbol{x},t). \tag{3.2}$$

Substitution into the time-dependent Schrödinger equation (1.2) yields the time-independent Schrödinger equation[2]

$$E\psi(\boldsymbol{x},E) = -\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{x},E) + V(\boldsymbol{x})\psi(\boldsymbol{x},E). \tag{3.3}$$

The potential on Figure 3.1 depends only on x. In this case we can also eliminate the derivatives with respect to y and z through further Fourier transformations,

$$\psi(\boldsymbol{x},E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk_2 \int_{-\infty}^{\infty} dk_3\, \exp[\mathrm{i}(k_2 y + k_3 z)]\,\psi(x,k_2,k_3,E)$$

[1]The normalization condition (1.20) implies that the function $\psi(\boldsymbol{x},E)$ does not exist in the sense of classical Fourier theory. We will therefore see in Section 5.2 that $\psi(\boldsymbol{x},E)$ is rather a series of δ-functions of the energy. This difficulty is usually avoided by using an *exponential ansatz* $\psi(\boldsymbol{x},t) = \psi(\boldsymbol{x},E)\exp(-\mathrm{i}Et/\hbar)$ instead of a full Fourier transformation. However, if one accepts the δ-function and corresponding extensions of classical Fourier theory, the transition to the time-independent Schrödinger equation through a formal Fourier transformation to the energy axis is logically more satisfactory.

[2]E. Schrödinger, Annalen Phys. 384, 361 (1926). Schrödinger found the time-indepedent equation first and published the time-dependent equation (1.2) five months later.

to find the time-independent Schrödinger equation for motion in the x direction,

$$E_1\psi(x,E_1) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,E_1) + V(x)\psi(x,E_1). \tag{3.4}$$

Here

$$E_1 \equiv E - \hbar^2\frac{k_2^2+k_3^2}{2m}, \quad \psi(x,E_1) \equiv \psi(x,k_2,k_3,E).$$

E_1 is the kinetic energy for motion in the x direction in the region $x<0$. Within each of the three separate regions $x<0$, $0<x<L$, and $x>L$ the potential attains a constant value, and equation (3.4) can be solved with a final Fourier transformation from x to k_1,

$$\psi(x,E_1) = \begin{cases} A\exp(\mathrm{i}k_1x) + B\exp(-\mathrm{i}k_1x), \;\; k_1 = \sqrt{2mE_1}/\hbar, \;\; x<0, \\ C\exp(\mathrm{i}k_1''x) + D\exp(-\mathrm{i}k_1''x), \\ \quad k_1'' = \sqrt{2m(E_1-\Phi_1)}/\hbar, \;\; 0<x<L, \\ F\exp(\mathrm{i}k_1'x) + G\exp(-\mathrm{i}k_1'x), \\ \quad k_1' = \sqrt{2m(E_1-\Phi_2)}/\hbar, \;\; x>L. \end{cases} \tag{3.5}$$

We must have $E_1 > 0$ because the absolute minimum of the potential determines a lower bound for the energy of a particle moving in the potential. However, the wavenumbers k_1'' and k_1' can be real or imaginary depending on the magnitude of E_1. We define

$$k_1'' = -\mathrm{i}\kappa, \quad k_1' = \mathrm{i}\kappa',$$

with the conventions $\kappa>0$, $\kappa'>0$, if k_1'' or k_1' are imaginary.
The wave function (3.5) is not yet the complete solution to our problem, because we have to impose junction conditions on the coefficients at the transition points $x=0$ and $x=L$ to ensure that the Schrödinger equation is also satisfied in those points. This will be done below. However, we can already discuss the meaning of the six different exponential terms appearing in (3.5). The wave function $\psi(x,E_1)$ is multiplied by the time-dependent exponential $\exp(-\mathrm{i}E_1t/\hbar)$ in the transition from $\psi(x,E_1)$ to the time-dependent wave function $\psi(x,t)$ for motion in x direction,

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}\hbar}\int_0^\infty dE_1\,\exp\left(-\frac{\mathrm{i}}{\hbar}E_1t\right)\psi(x,E_1). \tag{3.6}$$

A single monochromatic component therefore corresponds to a time-dependent wave funtion proportional to $\psi(x,E_1)\exp(-\mathrm{i}E_1t/\hbar)$. The term $A\exp[\mathrm{i}(k_1x - E_1t/\hbar)]$ corresponds to a right moving wave in the region $x<0$, while the term $B\exp[-\mathrm{i}(k_1x+E_1t/\hbar)]$ is a left moving wave. Similar identifications apply to the C and D components if k_1'' is real, and to the F and G components if k_1'

is real. Otherwise, these components will correspond to exponentially damped or growing wave functions, which requires $G = 0$ if $\kappa' = -\mathrm{i}k_1' > 0$ is real, to avoid divergence of the wave function for $x \to \infty$.

There is a subtle point here that needs to be emphasized because it is also relevant for potential scattering theory in three dimensions. We have just realized that the monochromatic wave function $\psi(x, E_1)$ describes a particle of energy E_1 (for the motion in x direction) simultaneously as left and right moving particles in the regions where the wave number is real. The energy dependent wave function always simultaneously describes all states of the particle with energy E_1, but does not yield a time resolved picture of what happens to a particle in the presence of the potential $V(x)$. Let us e.g. assume that we shoot a particle of energy E_1 at the potential $V(x)$ from the left. The component $A\exp[\mathrm{i}(k_1 x - E_1 t/\hbar)]$ describes the initially incident particle, while the component $B\exp[-\mathrm{i}(k_1 x + E_1 t/\hbar)]$ describes a particle that is reflected by the barrier. The component $F\exp[\mathrm{i}(k_1' x - E_1 t/\hbar)]$, on the other hand, describes a particle which went across the barrier (if $E_1 > \Phi_1$), or a particle that penetrated the barrier (without damaging the barrier!) if $\Phi_1 > E_1 > \Phi_2$.

The calculation of expectation values sheds light on the property of the monochromatic wave function $\psi(x, E_1)\exp(-\mathrm{i}E_1 t/\hbar)$ to describe all states of a particle of energy E_1 simultaneously. The expectation values both for location $\langle x\rangle$ and momentum $\langle p\rangle$ of a particle described by a monochromatic wave function are time-independent, i.e. a single monochromatic wave function can never describe the time evolution of a particle in the sense of first corresponding to an incident wave from the left, and later either to a reflected wave or a transmitted wave. A time resolved picture describing sequential events really requires superposition of several monochromatic components (3.6) with contributions from many different energies. Stated differently, the wave funcion of a particle can never correspond to only one exact value for the energy of the particle. Building realistic particle wave functions will always require superposition of different energy values, which corresponds to an uncertainty in the energy of the particle.

The monochromatic wave function can still tell us a lot about the behavior of particles in the presence of the potential barrier $V(x)$. We choose as an initial condition a particle moving against the barrier from the left. Then we have to set $G = 0$ in the solution above irrespective of whether k_1' is real or imaginary, because in the real case this component would correspond to a particle hitting the barrier from the right, and in the imaginary case $G = 0$ was imposed anyway from the requirement that the wave function cannot diverge.

Before we can proceed, we have to discuss junction conditions for wave functions at points where the potential is discontinuous.

A finite jump in $V(x)$ translates through the time-independent Schrödinger equation into a finite jump in $d^2\psi(x)/dx^2$, which means a jump in the slope, but not a discontinuity in $d\psi(x)/dx$. Therefore both $\psi(x)$ and $d\psi(x)/dx$ have

to remain continuous across a finite jump in the potential[3]. This means that the wave function $\psi(x)$ remains smooth across a finite jump in $V(x)$. On the other hand, an infinite jump in $V(x)$ only requires continuity, but not smoothness of $\psi(x)$.
The requirement of smoothness of the wave function yields the junction conditions

$$\begin{aligned} A + B &= C + D \\ k_1(A - B) &= k_1''(C - D) \\ C\exp(\mathrm{i}k_1''L) + D\exp(-\mathrm{i}k_1''L) &= F\exp(\mathrm{i}k_1'L) \\ k_1''[C\exp(\mathrm{i}k_1''L) - D\exp(-\mathrm{i}k_1''L)] &= k_1'F\exp(\mathrm{i}k_1'L) \end{aligned}$$

Elimination of C and D yields

$$\begin{aligned} 2k_1k_1''A &= \left[k_1''(k_1 + k_1')\cos(k_1''L) - \mathrm{i}(k_1k_1' + k_1''^2)\sin(k_1''L)\right] F\exp(\mathrm{i}k_1'L), \\ 2k_1k_1''B &= \left[k_1''(k_1 - k_1')\cos(k_1''L) - \mathrm{i}(k_1k_1' - k_1''^2)\sin(k_1''L)\right] F\exp(\mathrm{i}k_1'L). \end{aligned}$$

Note that

$$\cos(k_1''L) = \cosh(\kappa L), \quad \sin(k_1''L) = -\mathrm{i}\sinh(\kappa L).$$

If we decompose the wave function to the left and the right of the barrier into incoming, reflected, and transmitted components

$$\psi_{in}(x) = A\exp(\mathrm{i}k_1x), \quad \psi_{re}(x) = B\exp(-\mathrm{i}k_1x), \quad \psi_{tr}(x) = F\exp(\mathrm{i}k_1'x),$$

then the probability current density (1.18) yields

$$j_{in} = \frac{\hbar k_1}{m}|A|^2, \quad j_{re} = -\frac{\hbar k_1}{m}|B|^2, \quad j_{tr} = \frac{\hbar}{m}|F|^2\Re k_1'.$$

In the last equation we used that k_1' is either real or imaginary. The reflection and transmission coefficients from the barrier are then

$$R = \frac{|j_{re}|}{|j_{in}|} = \frac{|B|^2}{|A|^2}, \quad T = \frac{|j_{tr}|}{|j_{in}|} = \frac{|F|^2\Re k_1'}{|A|^2k_1}.$$

This yields in all cases $0 \le T = 1 - R \le 1$. The transmission coefficient is $T = 0$ for $0 < E_1 \le \Phi_2$,

$$\begin{aligned} T = {} & 4\sqrt{E_1(E_1 - \Phi_2)}(\Phi_1 - E_1) \\ & \times \left[(\Phi_1 - E_1)\left(2E_1 - \Phi_2 + 2\sqrt{E_1(E_1 - \Phi_2)}\right)\right. \\ & \left. + \Phi_1(\Phi_1 - \Phi_2)\sinh^2\left(\sqrt{2m(\Phi_1 - E_1)}L/\hbar\right)\right]^{-1} \end{aligned}$$

[3]The time-dependent Schrödinger equation permits discontinuous wave functions $\psi(x,t)$ even for smooth potentials, because there can be a trade-off between the derivative terms, see e.g. Problem 10.

for $\Phi_2 \leq E_1 \leq \Phi_1$, and

$$T = 4\sqrt{E_1(E_1-\Phi_2)}(E_1-\Phi_1) \times \left[(E_1-\Phi_1)\left(2E_1-\Phi_2+2\sqrt{E_1(E_1-\Phi_2)}\right) +\Phi_1(\Phi_1-\Phi_2)\sin^2\left(\sqrt{2m(E_1-\Phi_1)}L/\hbar\right)\right]^{-1}$$

for $E_1 \geq \Phi_1$. Classical mechanics, on the other hand predicts $T = 0$ for $E_1 < \Phi_1$ and $T = 1$ for $E_1 > \Phi_1$, in stark contrast to the quantum mechanical transmission coefficient shown in Figure 3.2.

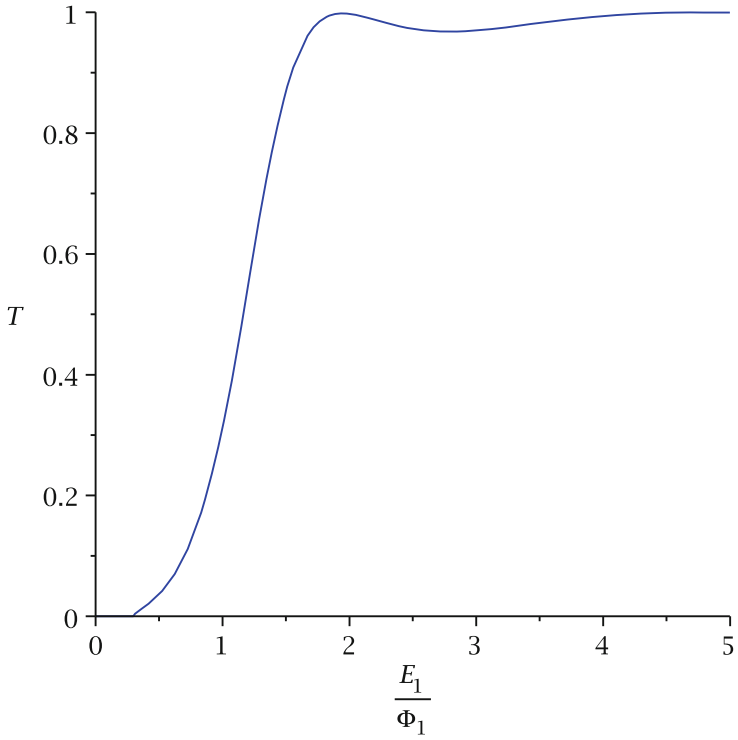


Figure 3.2: The transmission coefficient for a non-symmetric square barrier. The curve calculated here corresponds to $m = 511\,\mathrm{keV}/c^2$, $\Phi_1 = 10$ eV, $\Phi_2 = 3$ eV, $L = 2$ Å.

The phenomenon that particles can tunnel through regions even when they do not have the required energy is denoted as *tunnel effect*. It has been observed in many instances in nature and technology, e.g. in the α decay of radioactive nuclei (Gamow, 1928) or electron tunneling in heavily doped pn junctions (Esaki, 1958). Esaki diodes actually provide a beautiful illustration of the interplay of two quantum effects, viz. energy bands in solids and tunneling.

Charge carriers can tunnel from one energy band into a different energy band in heavily doped pn junctions. We will discuss energy bands in Chapter 10. Quantum mechanical tunneling is also used e.g. in scanning tunneling microscopes (Binnig & Rohrer, 1982), and in flash memory and magnetic tunnel junction devices[4].

It is easy to understand from our results for the transmission probability why quantum mechanical tunneling plays such an important role in modern memory devices. If we want to have a memory device which is electrically controlled, then apparently the information bits 0 and 1 can be encoded through the two states of a device being electrically charged or neutral. If we also want to maintain storage of the information even when the power supply is switched off (a *non-volatile memory*), then the device should not discharge spontaneously, i.e. it should be electrically insulated. The device should therefore be a conductor which is surrounded by insulating material. Such a device is called a *floating gate* in flash memory devices see Figure 3.3.

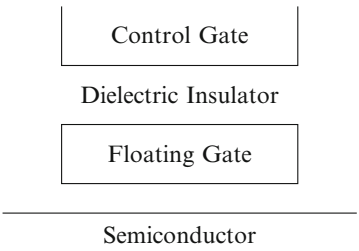


Figure 3.3: A simplified schematic of a flash memory cell. The tunneling barrier is the thin section of the insulator between the floating gate and the semiconductor.

However, we do want to be able to charge or discharge the floating gate, i.e. eventually we want to run a current through the surrounding insulator without destroying the insulator. Using a tunneling current through the insulator is an elegant way to achieve this. Our results for the tunneling probability tell us how to switch a tunneling current. If we substitute $m = 511$ keV$/c^2$, $\Phi_1 - E_1 \simeq 1$ eV, and $L \simeq 10$ nm, we find

$$\sqrt{2m(\Phi_1 - E_1)}L/\hbar \simeq 51$$

and therefore

$$\sinh^2\Big(\sqrt{2m(\Phi_1 - E_1)}L/\hbar\Big) \simeq \frac{1}{4}\exp\Big(2\sqrt{2m(\Phi_1 - E_1)}L/\hbar\Big),$$

[4]Magnetic tunnel junctions provide yet another beautiful example of the interplay of two quantum effects – tunneling and exchange interactions. Exchange interactions will be discussed in Chapter 17.

i.e. in excellent approximation

$$T \simeq 16\frac{\sqrt{E_1(E_1-\Phi_2)}(\Phi_1-E_1)}{\Phi_1(\Phi_1-\Phi_2)}\exp\Big(-2\sqrt{2m(\Phi_1-E_1)}L/\hbar\Big).$$

The exponential dependence on $\sqrt{\Phi_1 - E_1}$ implies that decreasing $\Phi_1 - E_1$ by increasing E_1 will have a huge impact on the tunneling current through the insulator. We can control the energy E_1 of the electrons in the floating gate through the electron concentration in a nearby control gate. Presence of a negative charge on the nearby control gate will increase the energy of any electrons stored in the floating gate and allow them to tunnel into a conducting sink (usually a semiconductor) opposite to the control gate. This process will discharge the floating gate. On the other hand, a positive charge on the control gate will attract electrons from an electron current through the semiconductor towards the insulating barrier and help them to tunnel into the floating gate.

3.2 Box approximations for quantum wells, quantum wires and quantum dots

A particle in three dimensions which can move freely in two directions, but is confined in one direction, is said to be confined in a quantum well. A particle which can move freely only in one direction but is confined in two directions is confined in a quantum wire. Finally, a particle which is confined to a small region of space is confined to a quantum dot. We will discuss energy levels and wave functions of particles in all three situations in the approximation of confinement to rectangular (box-like) regions. For the quantum well this means that our particle will be confined to the region $0 < x < L_1$, but it can move freely in y and z direction. The particle in the quantum wire is confined in x and y direction to $0 < x < L_1$, $0 < y < L_2$, but it can move freely in the z direction. Finally, box approximation for a quantum dot means that the particle is confined to the box $0 < x < L_1$, $0 < y < L_2$, $0 < z < L_3$.
We will assume strict confinement in this section, i.e. the wave function of the particle vanishes outside of the allowed region while the wave function inside the region must continuously go to zero at the boundaries of the allowed region. We gauge the energy axis such that in the allowed region the potential energy of the particle vanishes, $V(\boldsymbol{x}) = 0$, i.e. the time-independent three-dimensional Schrödinger equation in the allowed region takes the form

$$E\psi(\boldsymbol{x}) = -\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{x}). \tag{3.7}$$

Substitution of the Fourier decomposition

$$\psi(\boldsymbol{x}) = \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\,\psi(\boldsymbol{k})\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})$$

yields $k = \sqrt{2mE}/\hbar$ and the general solution for given energy E takes the form

$$\psi(\boldsymbol{x}) = \int d^2\hat{\boldsymbol{k}}\, A(\hat{\boldsymbol{k}}) \exp\left(\frac{\mathrm{i}}{\hbar}\sqrt{2mE}\hat{\boldsymbol{k}}\cdot\boldsymbol{x}\right), \quad \hat{\boldsymbol{k}}^2 = 1.$$

On the other hand, equation (3.7) tells us that the energy of a plane wave $\psi(\boldsymbol{x}) = \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})/\sqrt{2\pi}^3$ of momentum $\boldsymbol{p} = \hbar\boldsymbol{k}$ is

$$E = \frac{\hbar^2\boldsymbol{k}^2}{2m}. \tag{3.8}$$

If we have no confinement condition at all, our particle is a free particle and equation (3.8) is the kinetic energy of a free non-relativistic particle of momentum $\boldsymbol{p} = \hbar\boldsymbol{k}$.

Energy levels in a quantum well

If we have a confinement condition in x-direction, $\psi(0, y, z) = 0$ and $\psi(L_1, y, z) = 0$, then we have to superimpose plane wave solutions in x direction to form a standing wave with nodes at the boundary points, and we find solutions

$$\psi_{n_1,k_2,k_3}(\boldsymbol{x}) = \frac{1}{\pi\sqrt{2L_1}} \exp[\mathrm{i}(k_2 y + k_3 z)] \sin\left(\frac{n_1\pi x}{L_1}\right), \tag{3.9}$$

with integer $n_1 \in \mathbb{N}$ and energy

$$E_{n_1,k_2,k_3} = \frac{\hbar^2}{2m}\left(k_2^2 + k_3^2 + \frac{n_1^2\pi^2}{L_1^2}\right).$$

The energy of the particle is therefore determined by the discrete quantum number n_1 and the continuous wave numbers k_2 and k_3.

Energy levels in a quantum wire

If the particle is confined both in the x-direction to the region $0 < x < L_1$ and in the y-direction to the region $0 < y < L_2$, the boundary conditions $\psi(0, y, z) = 0$, $\psi(L_1, y, z) = 0$, $\psi(x, 0, z) = 0$ and $\psi(x, L_2, z) = 0$ yield

$$\psi_{n_1,n_2,k_3}(\boldsymbol{x}) = \sqrt{\frac{2}{\pi L_1 L_2}} \exp(\mathrm{i}k_3 z) \sin\left(\frac{n_1\pi x}{L_1}\right) \sin\left(\frac{n_2\pi x}{L_2}\right), \tag{3.10}$$

and the energy of the particle is determined by the discrete quantum numbers n_1 and n_2 and the continuous wave number k_3 for motion in z direction,

$$E_{n_1,n_2,k_3} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right) + \frac{\hbar^2 k_3^2}{2m}.$$

Energy levels in a quantum dot

If the particle is confined to the region $0 < x < L_1$, $0 < y < L_2$, $0 < z < L_3$, the conditions of vanishing wave function on the boundaries yields normalized states

$$\psi_{n_1,n_2,n_3}(\boldsymbol{x}) = \sqrt{\frac{8}{L_1 L_2 L_3}} \sin\left(\frac{n_1 \pi x}{L_1}\right) \sin\left(\frac{n_2 \pi y}{L_2}\right) \sin\left(\frac{n_3 \pi z}{L_3}\right), \tag{3.11}$$

and the energy levels are determined in terms of three discrete quantum numbers,

$$E_{n_1,n_2,n_3} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right). \tag{3.12}$$

Degeneracy of quantum states

If two or more different quantum states have the same energy, the quantum states are said to be degenerate, and the corresponding energy level is also denoted as degenerate. This happens e.g. for the quantum wire and the quantum dot if at least two of the length scales L_i have the same value. We will discuss the quantum dot (3.12,3.11) with $L_1 = L_2 = L_3 \equiv L$ as an example. This cubic quantum dot has energy levels

$$E_{n_1,n_2,n_3} = \left(n_1^2 + n_2^2 + n_3^2\right) \frac{\pi^2 \hbar^2}{2mL^2}.$$

The lowest energy level

$$E_{1,1,1} = 3\frac{\pi^2 \hbar^2}{2mL^2}$$

corresponds to a unique quantum state $\psi_{1,1,1}(\boldsymbol{x})$ and is therefore non-degenerate. However, the next allowed energy value

$$E_{1,1,2} = E_{1,2,1} = E_{2,1,1} = 6\frac{\pi^2 \hbar^2}{2mL^2}$$

is realized for three different wave functions $\psi_{1,1,2}(\boldsymbol{x})$, $\psi_{1,2,1}(\boldsymbol{x})$ and $\psi_{2,1,1}(\boldsymbol{x})$, and is therefore *three-fold degerate*. Three-fold degeneracy is also realized for the next two energy levels

$$E_{1,2,2} = E_{2,1,2} = E_{2,2,1} = 9\frac{\pi^2 \hbar^2}{2mL^2}$$

and

$$E_{1,1,3} = E_{1,3,1} = E_{3,1,1} = 11\frac{\pi^2 \hbar^2}{2mL^2}.$$

The next energy level is again non-degenerate,

$$E_{2,2,2} = 12\frac{\pi^2\hbar^2}{2mL^2}.$$

Then follows a six-fold degenerate energy level,

$$E_{1,2,3} = E_{2,3,1} = E_{3,1,2} = E_{1,3,2} = E_{3,2,1} = E_{2,1,3} = 14\frac{\pi^2\hbar^2}{2mL^2}.$$

3.3 The attractive δ function potential

The attractive δ function potential

$$V(x) = -\mathcal{W}\delta(x), \quad \mathcal{W} > 0,$$

provides a simple model system for co-existence of free states and bound states of particles in a potential.
Positive energy solutions of the stationary Schrödinger equation for the δ function potential must have the form

$$\psi_k(x) = \sum_{\pm} \Theta(\pm x)\left[A_\pm \exp(\mathrm{i}kx) + B_\pm \exp(-\mathrm{i}kx)\right], \quad \hbar k = \sqrt{2mE},$$

and nomalizability limits the negative energy solutions to the from

$$\psi_\kappa(x) = \sum_{\pm} \Theta(\pm x) C_\pm \exp(\mp\kappa x), \quad \hbar\kappa = \sqrt{-2mE}.$$

These solutions must be continuous in order not to generate $\delta'(x)$ terms wich would violate the Schrödinger equation,

$$A_+ + B_+ = A_- + B_-, \quad C_+ = C_-. \tag{3.13}$$

On the other hand, integrating the Schrödinger equation from $x = -\epsilon$ to $x = \epsilon$ and taking the limit $\epsilon \to 0+$ yields the junction conditions

$$\lim_{\epsilon\to 0+}\left(\left.\frac{d\psi(x)}{dx}\right|_{x=\epsilon} - \left.\frac{d\psi(x)}{dx}\right|_{x=-\epsilon}\right) = -\frac{2m}{\hbar^2}\mathcal{W}\psi(0),$$

i.e.

$$\mathrm{i}k(A_+ - B_+ - A_- + B_-) = -\frac{m}{\hbar^2}\mathcal{W}(A_+ + B_+ + A_- + B_-) \tag{3.14}$$

for the free states and

$$\kappa = \frac{m}{\hbar^2}\mathcal{W} \tag{3.15}$$

for the bound states.
Equation (3.15) tells us that there exists one bound state for $\mathcal{W} > 0$ with energy

$$E_\kappa = -\frac{m}{2\hbar^2}\mathcal{W}^2.$$

The normalized bound state is

$$\psi_\kappa(x) = \sqrt{\kappa}\exp(-\kappa|x|). \tag{3.16}$$

For the free states, we first look at solutions which are right or left moving plane waves $\exp(\pm \mathrm{i}kx)/\sqrt{2\pi}$ on the half-line $x > 0$, i.e. we solve equations (3.13) and (3.14) first under the conditions $A_+ = 1/\sqrt{2\pi}$, $B_+ = 0$, and then under the conditions $A_+ = 0$, $B_+ = 1/\sqrt{2\pi}$. This yields solutions

$$\psi_k(x) = \frac{1}{\sqrt{2\pi}}\exp(\mathrm{i}kx) + \sqrt{\frac{2}{\pi}}\Theta(-x)\frac{\kappa}{k}\sin(kx),$$

$$\psi_{-k}(x) = \frac{1}{\sqrt{2\pi}}\exp(-\mathrm{i}kx) + \sqrt{\frac{2}{\pi}}\Theta(-x)\frac{\kappa}{k}\sin(kx).$$

The free solutions can be unified if we also allow for negative values of k (recall that up to now k was defined positive from $\hbar k = \sqrt{2mE}$),

$$\psi_k(x) = \frac{1}{\sqrt{2\pi}}\exp(\mathrm{i}kx) + \sqrt{\frac{2}{\pi}}\Theta(-x)\frac{\kappa}{k}\sin(kx). \tag{3.17}$$

The solution for $B_+ = 0$ can be used to read off the reflection and transmission coefficients for the δ function potential,

$$R = \left|\frac{B_-}{A_-}\right|^2 = \frac{\kappa^2}{k^2+\kappa^2} = \frac{B}{E+B}, \quad T = \left|\frac{A_+}{A_-}\right|^2 = \frac{k^2}{k^2+\kappa^2} = \frac{E}{E+B}.$$

Here $B \equiv -E_\kappa$ is the binding energy of the bound state.
In many situations it is also convenient to use even and odd solutions of the Schrödinger equation. Odd (or *negative parity*) solutions $\psi(x) = -\psi(-x)$ must satisfy $A_+ = -B_-$, $B_+ = -A_-$. Solving equations (3.13) and (3.14) with these conditions yields the negative parity solutions

$$\psi_{k,-}(x) = \frac{1}{\sqrt{\pi}}\sin(kx). \tag{3.18}$$

The positive energy solutions of positive parity follow from $A_+ = B_-$, $B_+ = A_-$ and equations (3.13), (3.14) in the form

$$\psi_{k,+}(x) = \frac{1}{\sqrt{\pi}}\frac{k\cos(kx) - \kappa\sin(k|x|)}{\sqrt{\kappa^2+k^2}}. \tag{3.19}$$

The wave number k in (3.18) and (3.19) is constrained to the positive half-line $k = \sqrt{2mE}/\hbar > 0$.
The solutions (3.16), (3.18) and (3.19) satisfy the usual orthonormalization conditions for bound or free states, respectively, and the completeness relation

$$\psi_\kappa(x)\psi_\kappa(x') + \int_0^\infty dk\,[\psi_{k,-}(x)\psi_{k,-}(x') + \psi_{k,+}(x)\psi_{k,+}(x')] = \delta(x-x'). \quad (3.20)$$

There is no bound state solution for a repulsive δ potential

$$V(x) = \mathcal{W}\delta(x) = \frac{\hbar^2\kappa}{m}\delta(x)$$

and the even parity energy eigenstates become

$$\phi_{k,+}(x) = \frac{1}{\sqrt{\pi}}\frac{k\cos(kx) + \kappa\sin(k|x|)}{\sqrt{\kappa^2 + k^2}}.$$

The completeness relation for the eigenfunctions of the repulsive δ potential is therefore

$$\int_0^\infty dk\,[\psi_{k,-}(x)\psi_{k,-}(x') + \phi_{k,+}(x)\phi_{k,+}(x')] = \delta(x - x'). \quad (3.21)$$

3.4 Evolution of free Schrödinger wave packets

Another important model system for quantum behavior is provided by free wave packets. We will discuss in particular free Gaussian wave packets, because they provide a simple analytic example for dispersion of free wave packets.

The free Schrödinger propagator

Substitution of a Fourier *ansatz*

$$\psi(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} d\omega\,\psi(k,\omega)\exp[\mathrm{i}(kx - \omega t)]$$

into the free Schrödinger eqation shows that the general solution of that equation in one dimension is given in terms of a wave packet

$$\psi(k,\omega) = \sqrt{2\pi}\psi(k)\delta\left(\omega - \frac{\hbar k^2}{2m}\right),$$

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\,\psi(k)\exp\left[\mathrm{i}\left(kx - \frac{\hbar k^2}{2m}t\right)\right]. \quad (3.22)$$

The amplitude $\psi(k)$ is connected to the initial condition $\psi(x,0)$ through inverse Fourier transformation

$$\psi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, \psi(x,0) \exp(-\mathrm{i}kx)\,,$$

and substitution of $\psi(k)$ into (3.22) leads to the expression

$$\psi(x,t) = \int_{-\infty}^{\infty} dx'\, U(x-x',t)\psi(x',0) \tag{3.23}$$

with the free *propagator*

$$U(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, \exp\left[\mathrm{i}\left(kx - \frac{\hbar k^2}{2m}t\right)\right]. \tag{3.24}$$

This is sometimes formally integrated as[5]

$$U(x,t) = \sqrt{\frac{m}{2\pi \mathrm{i}\hbar t}} \exp\left(\mathrm{i}\frac{mx^2}{2\hbar t}\right). \tag{3.25}$$

The propagator is the particular solution of the free Schrödinger equation

$$\mathrm{i}\hbar \frac{\partial}{\partial t} U(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} U(x,t)$$

with initial condition $U(x,0) = \delta(x)$. It yields the corresponding *retarded Green's function*

$$\mathrm{i}\hbar \frac{\partial}{\partial t} \mathcal{G}(x,t) + \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \mathcal{G}(x,t) = \delta(t)\delta(x), \tag{3.26}$$

$$\mathcal{G}(x,t)\Big|_{t<0} = 0, \tag{3.27}$$

through

$$\mathcal{G}(x,t) = \frac{\Theta(t)}{\mathrm{i}\hbar} U(x,t). \tag{3.28}$$

This can also be derived from the Fourier decomposition of equation (3.26), which yields

$$\mathcal{G}(x,t) = \frac{1}{(2\pi)^2 \hbar} \int_{-\infty}^{\infty} dk \int_{-\infty}^{\infty} d\omega\, \frac{\exp[\mathrm{i}(kx - \omega t)]}{\omega - (\hbar k^2/2m) + \mathrm{i}\epsilon}.$$

The negative imaginary shift of the pole $(\hbar k^2/2m) - \mathrm{i}\epsilon$, $\epsilon \to +0$, in the complex ω plane ensures that the condition (3.27) is satisfied. We will encounter time evolution operators and Green's functions in many places in this book. The designation *propagator* is often used both for the time evolution operator $U(x,t)$ and for the related Green's function $\mathcal{G}(x,t)$. $U(x,t)$ propagates initial conditions as in equation (3.23), and we will later see in many examples that $\mathcal{G}(x,t)$ propagates perturbations or source terms in the Schrödinger equation.

[5] The propagator is commonly denoted as $K(x,t)$. However, we prefer the notation $U(x,t)$ because the propagator is nothing but the x representation of the time evolution operator $U(t)$ introduced in Chapter 13.

Width of Gaussian wave packets

A wave packet $\psi(x,t)$ is denoted as a *Gaussian wave packet* if $|\psi(x,t)|^2$ is a Gaussian function of x. We will see below through direct Fourier transformation that $\psi(x,t)$ is a Gaussian wave packet in x if and only if $\psi(k,t)$ is a Gaussian wave packet in k.
Normalized Gaussian wave packets have the general form

$$\psi(x,t) = \left(\frac{2\alpha(t)}{\pi}\right)^{\frac{1}{4}} \exp\bigl(-\alpha(t)[x - x_0(t)]^2 + \mathrm{i}\varphi(x,t)\bigr), \tag{3.29}$$

and we will verify that the real coefficient $\alpha(t)$ is related to the variance through $\Delta x^2(t) = 1/4\alpha(t)$. The expectation values of x and x^2 are readily evaluated,

$$\begin{aligned}\langle x\rangle(t) &= \sqrt{\frac{2\alpha(t)}{\pi}} \int_{-\infty}^{\infty} dx\, x \exp\bigl(-2\alpha(t)[x - x_0(t)]^2\bigr) \\ &= \sqrt{\frac{2\alpha(t)}{\pi}} \int_{-\infty}^{\infty} d\xi\, [\xi + x_0(t)] \exp\bigl(-2\alpha(t)\xi^2\bigr) = x_0(t),\end{aligned}$$

$$\begin{aligned}\langle x^2\rangle(t) &= \sqrt{\frac{2\alpha(t)}{\pi}} \int_{-\infty}^{\infty} dx\, x^2 \exp\bigl(-2\alpha(t)[x - x_0(t)]^2\bigr) \\ &= \sqrt{\frac{2\alpha(t)}{\pi}} \int_{-\infty}^{\infty} d\xi\, [\xi + x_0(t)]^2 \exp\bigl(-2\alpha(t)\xi^2\bigr) \\ &= \sqrt{\frac{2\alpha(t)}{\pi}} \left(x_0^2(t) - \frac{1}{2}\frac{d}{d\alpha(t)}\right) \int_{-\infty}^{\infty} d\xi\, \exp\bigl(-2\alpha(t)\xi^2\bigr) \\ &= x_0^2(t) + \frac{1}{4\alpha(t)},\end{aligned}$$

and therefore we find indeed

$$\Delta x^2(t) = \langle x^2\rangle(t) - \langle x\rangle^2(t) = \frac{1}{4\alpha(t)}. \tag{3.30}$$

Free Gaussian wave packets in Schrödinger theory

We assume that the wave packet at time $t = 0$ was a Gaussian wave packet of width Δx,

$$\psi(x,0) = \frac{1}{(2\pi\Delta x^2)^{1/4}} \exp\left(-\frac{(x - x_0)^2}{4\Delta x^2} + \mathrm{i}k_0 x\right). \tag{3.31}$$

This yields a Gaussian wave packet of constant width

$$\Delta k = \frac{1}{2\Delta x}$$

in k space,

$$\begin{aligned}\psi(k) &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dx\, \psi(x,0)\exp(-\mathrm{i}kx)\\ &= \frac{1}{(2\pi)^{3/4}(\Delta x^2)^{1/4}}\int_{-\infty}^{\infty} dx\, \exp\left(-\frac{(x-x_0)^2}{4\Delta x^2}+\mathrm{i}(k_0-k)x\right)\\ &= \frac{1}{(2\pi)^{3/4}(\Delta x^2)^{1/4}}\exp[\mathrm{i}(k_0-k)x_0]\int_{-\infty}^{\infty} d\xi\, \exp\left[-\frac{\xi^2}{4\Delta x^2}+\mathrm{i}(k_0-k)\xi\right]\\ &= \left(\frac{2\Delta x^2}{\pi}\right)^{\frac{1}{4}}\exp\left[-\Delta x^2(k-k_0)^2-\mathrm{i}(k-k_0)x_0\right], \end{aligned} \tag{3.32}$$

$$\psi(k,t) = \psi(k)\exp\left(-\mathrm{i}\frac{\hbar k^2}{2m}t\right). \tag{3.33}$$

Substitution of $\psi(k)$ into equation (3.22) then yields

$$\begin{aligned}\psi(x,t) &= \left(\frac{\Delta x^2}{2\pi^3}\right)^{\frac{1}{4}}\exp\left(-\Delta x^2k_0^2+\mathrm{i}k_0x_0\right)\\ &\quad\times\int_{-\infty}^{\infty} dk\, \exp\left[-\left(\Delta x^2+\mathrm{i}\frac{\hbar t}{2m}\right)k^2+\left(2\Delta x^2k_0+\mathrm{i}(x-x_0)\right)k\right]\\ &= \frac{(2\pi\Delta x^2)^{1/4}}{\left[2\pi\Delta x^2+\mathrm{i}\pi(\hbar t/m)\right]^{1/2}}\exp\left(-\Delta x^2k_0^2+\mathrm{i}k_0x_0\right)\\ &\quad\times\exp\left[\frac{\left[2\Delta x^2k_0+\mathrm{i}(x-x_0)\right]^2}{4\Delta x^2+2\mathrm{i}(\hbar t/m)}\right]\\ &= \frac{(2\pi\Delta x^2)^{1/4}}{\left[2\pi\Delta x^2+\mathrm{i}\pi(\hbar t/m)\right]^{1/2}}\exp\left[-\frac{\left[x-x_0-(\hbar k_0/m)t\right]^2}{4\Delta x^2+(\hbar^2t^2/m^2\Delta x^2)}\right]\\ &\quad\times\exp\left[\mathrm{i}\left(k_0x-\frac{\hbar k_0^2}{2m}t+\frac{\hbar t}{8m}\frac{\left[x-x_0-(\hbar k_0/m)t\right]^2}{(\Delta x^2)^2+(\hbar^2t^2/4m^2)}\right)\right]. \end{aligned} \tag{3.34}$$

Comparison of equation (3.34) with equations (3.29,3.30) yields

$$\Delta x^2(t) = \Delta x^2+\frac{\hbar^2t^2}{4m^2\Delta x^2}, \tag{3.35}$$

i.e. a strongly localized packet at time $t=0$ will disperse very fast, because the dispersion time scale τ is proportional to Δx^2. The reason for the fast dispersion is that a strongly localized packet at $t=0$ comprises many different wavelengths. However, each monochromatic component in a free wave packet travels with its own phase velocity

$$v(k) = \frac{\omega}{k} = \frac{\hbar k}{2m},$$

and a free strongly localized packet therefore had to emerge from rapid collapse and will disperse very fast. On the other hand, a poorly localized packet is almost monochromatic and therefore slowly changes in shape.

The relevant time scale for decay of the wave packet is

$$\tau = \frac{2m\Delta x^2}{\hbar}. \tag{3.36}$$

For a particle of mass $m = 1\,\mathrm{g}$ and an extension $\Delta x = 1\,\mathrm{cm}$ this yields a time scale

$$\tau \simeq 2 \times 10^{27}\,\mathrm{s}$$

which is about five billion times the age of the universe. But for an electron wave packet with $\Delta x = 1\,\text{Å}$ this yields an extremely short time scale

$$\tau \simeq 2 \times 10^{-16}\,\mathrm{s},$$

which means that the wave function of that free electron would be smeared across the observable universe within a few minutes. This reveals one of the limitations of single particle interpretations in quantum mechanics. In particular, our notion of elementary particles as autonomous entities which can exist by themselves is useful for many situations, but not entirely correct. Starting in Chapter 17, we will see that particles are excitations of quantum fields in continuous interaction. Starting in Chapter 18, and in particular in Chapter 21, we will see that relativistic quantum mechanics does not permit strict single particle solutions, but particles always excite their corresponding antiparticles. For the wave packet (3.31) this means that a positron component ϕ in the wave function is not negligibe any more relative to the electron wave function ψ at a distance of order

$$d \simeq \frac{4mc}{\hbar}\Delta x^2 \simeq 10^4\,\mathrm{nm}^{-1}\Delta x^2 = 10^{11}\,\mathrm{cm}^{-1}\Delta x^2. \tag{3.37}$$

This implies that we cannot use the wave packet for a strongly localized free electron with $\Delta x = 1\,\text{Å}$ beyond a distance of about $0.1\,\mu\mathrm{m}$.

We will see in Chapters 6 and 7 that wave packets can remain localized under the influence of forces, i.e. the notion of stable electrons in atoms makes sense, although the notion of highly localized *free* electrons governed by the *free* Schrödinger equation is apparently limited to not too large distance and time scales.

We can infer from the example of the free Gaussian wave packet that the kinetic term in the Schrödinger equation drives wave packets apart. If there is no attractive potential term, the kinetic term decelerates any eventual initial contraction of a free wave packet and ultimately pushes the wave packet towards accelerated dispersion. We will see that this action of the kinetic term can be compensated by attractive potential terms in the Schrödinger equation. Balance between the collapsing force from attractive potentials and the dispersing force from the kinetic term can stabilize quantum systems.

Comparison of equation (3.33) with equations (3.29,3.30) yields constant width of the wave packet in k space and therefore

$$\Delta p = \hbar\Delta k = \frac{\hbar}{2\Delta x},$$

i.e. there is no dispersion in momentum. The product of uncertainties of momentum and location of the particle satisfies $\Delta p \Delta x(t) \geq \hbar/2$, in agreement with Heisenberg's uncertainty relation, which will be derived for general wave packets in Section 5.1.
The energy expectation value and uncertainty of the wave packet are

$$\langle E \rangle = \frac{\hbar^2}{2m}\left(k_0^2 + \frac{1}{4\Delta x^2}\right)$$

and

$$\Delta E = \frac{\hbar^2}{2m}\sqrt{\frac{k_0^2}{\Delta x^2} + \frac{1}{8\Delta x^4}}.$$

Suppose we want to observe strong localization of a free particle. The decay time (3.36) then defines a measure for the time window Δt of observability of the particle. This satisfies

$$\Delta E \Delta t = \hbar\sqrt{\frac{1}{8} + k_0^2 \Delta x^2} \geq \frac{\hbar}{\sqrt{8}},$$

in agreement with the qualitative energy-time uncertainty relation (5.7), which we will encounter in Section 5.1.
The free Gaussian wave packet reproduces momentum eigenstates in the limit $\Delta x^2 \to \infty$ in the sense

$$\lim_{\Delta x^2 \to \infty}\left(\frac{\Delta x^2}{2\pi}\right)^{1/4} \psi(k) = \delta(k - k_0),$$

$$\lim_{\Delta x^2 \to \infty}\left(\frac{\Delta x^2}{2\pi}\right)^{1/4} \psi(x,t) = \frac{1}{\sqrt{2\pi}} \exp\left[\mathrm{i}\left(k_0 x - \frac{\hbar t}{2m}k_0^2\right)\right].$$

3.5 Problems

3.1 Show that the tunneling probability for the square barrier in Figure 3.1 always satisfies $T < 1$ if $\Phi_2 > 0$.
Remark: Don't be fooled by Figure 3.2. The first transmission maximum at $E_1 \simeq 2\Phi_1$ corresponds already to $T \simeq 0.998$ and the next transmission maximum is even closer to 1, but it only looks like the tansmission probability would reach 1 in Figure 3.2.
Tunneling resonances $T = 1$ occur for $\Phi_2 = 0$. For which values of E_1 and k_1 do this tunneling resonances occur? Which geometric matching condition holds between the wavelength of the incident particles and the square barrier for the tunneling resonances?

3.2 A barrier for motion of a particle consists of a combination of two repulsive δ function potentials with separation a,

$$V(x) = \mathcal{W}\delta(x) + \mathcal{W}\delta(x - a).$$

Calculate the reflection and transmission coefficients for particles with momentum $\hbar k$.

3.3 Why is there a simple relation between momentum uncertainty and energy level in the box model for a quantum dot? What is the relation?

3.4 A very simple cubic model for a color center in an alkali halide crystal consists of an electron confined to a cube of length L. How large is the length L if the electron absorbs photons of energy 2.3 eV?
Mollwo had found the empirical relation $\nu d^2 = 5.02 \times 10^{-5}\,\mathrm{m^2Hz}$ between absorption frequencies ν of color centers and lattice constants d in alkali halide crystals. For the simple cubic model, which relation between L and d follows from Mollwo's relation?
A spherical model is also very simple, but gives a better estimate for the ratio between size of the color center and lattice constant, see the corresponding problem in Chapter 7.

3.5 Calculate the momentum uncertainty in the bound state (3.16).

3.6 Show that all the momentum expectation values $\langle p^n \rangle$ are conserved for a free particle.
If the particle is moving in a potential $V(x)$, find a necessary and sufficient condition for $V(x)$ such that $\langle p^n \rangle$ is constant.

3.7 Suppose $\psi(x,t)$ is a normalizable free wave packet in one dimension, e.g. the Gaussian wave packet from Section 3.4. Which classical quantity of the particle corresponds to the integral $\int dx\, j(x)$ of the current density? Does a similar result hold for $\int d^3\boldsymbol{x}\, \boldsymbol{j}(\boldsymbol{x})$ in three dimensions?

3.8 The wave function of a free particle at time $t = 0$ is

$$\psi(x,0) = \sqrt{\frac{2a^3}{\pi}}\frac{1}{x^2 + a^2}.$$

How large are the uncertainties $\Delta x(t)$ and Δp in location and momentum of the particle?
Remark: The wave function $\psi(x,t)$ of the particle can be expressed in terms of complex error functions, but it is easier to use the wave function $\psi(k,t)$ in k space for the calculation of the uncertainties.

3.9 The wave function of a free particle at time $t = 0$ is

$$\psi(x,0) = \sqrt{\kappa}\exp(-\kappa|x|)\,. \tag{3.38}$$

One could produce this state as initial state of a free particle by first capturing the particle in the bound state of an attractive δ potential and then switching off the potential.
Calculate the wave function $\psi(k,t)$ of the particle.
How large are the uncertainties $\Delta x(t)$ and Δp in location and momentum of the particle?

3.10 The wave function of a free particle at time $t = 0$ is

$$\psi(x,0) = \frac{\Theta(x+a)\Theta(a-x)}{\sqrt{2a}} = \frac{\Theta(a-x) - \Theta(-x-a)}{\sqrt{2a}} = \frac{\Theta(x+a) - \Theta(x-a)}{\sqrt{2a}}. \tag{3.39}$$

Calculate the wave function $\psi(x,t)$ of the particle.

Solution to Problem 10
The wave function in momentum space is

$$\psi(k) = \frac{1}{2\sqrt{\pi a}} \int_{-a}^{a} dx\, \exp(-\mathrm{i}kx) = \frac{\sin(ka)}{\sqrt{\pi a}k},$$

$$\psi(k,t) = \psi(k) \exp\left(-\mathrm{i}\frac{\hbar k^2}{2m}t\right).$$

The wave function $\psi(x,t)$ can be evaluated numerically from the first line of the following representations,

$$\begin{aligned}\psi(x,t) &= \frac{1}{2\pi\mathrm{i}\sqrt{2a}} \int_{-\infty}^{\infty} dk\, \frac{\exp[\mathrm{i}k(x+a)] - \exp[\mathrm{i}k(x-a)]}{k} \exp\left(-\mathrm{i}\frac{\hbar t}{2m}k^2\right) \\ &= \frac{1}{2\pi\mathrm{i}\sqrt{2a}} \int_{-\infty}^{\infty} dk\, \frac{\exp[\mathrm{i}k(x+a)] - \exp[\mathrm{i}k(x-a)]}{k+\mathrm{i}\epsilon} \exp\left(-\mathrm{i}\frac{\hbar t}{2m}k^2\right) \\ &= \frac{1}{2\pi\mathrm{i}\sqrt{2a}} \int_{-\infty}^{\infty} dk\, \frac{\exp[\mathrm{i}k(x+a)] - \exp[\mathrm{i}k(x-a)]}{k-\mathrm{i}\epsilon} \exp\left(-\mathrm{i}\frac{\hbar t}{2m}k^2\right).\end{aligned}$$

However, we can also proceed with the analytical evaluation of the integrals by using the observation

$$\pm\frac{\partial}{\partial a} \int_{-\infty}^{\infty} dk\, \frac{\exp[\mathrm{i}k(x\pm a)]}{k} \exp\left(-\mathrm{i}\frac{\hbar t}{2m}k^2\right) = \mathrm{i}\sqrt{\frac{2\pi m}{\mathrm{i}\hbar t}} \exp\left(\mathrm{i}\frac{m}{2\hbar t}(x\pm a)^2\right).$$

Integration with respect to the parameter a then yields

$$\psi(x,t) = \frac{1}{2\sqrt{2a}} \left[\mathrm{erf}\left(\sqrt{\frac{m}{2\mathrm{i}\hbar t}}(x+a)\right) - \mathrm{erf}\left(\sqrt{\frac{m}{2\mathrm{i}\hbar t}}(x-a)\right)\right], \tag{3.40}$$

where the error function is defined as

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z du\, \exp(-u^2).$$

One can easily check that the error functions $\mathrm{erf}[\sqrt{m/2\mathrm{i}\hbar t}(x-x_0)]$ satisfy the free Schrödinger equation. The wave function $\psi(x,t)$ from equation (3.40) also satisfies the initial condition (3.39) through

$$\lim_{t\to 0-\mathrm{i}\epsilon} \mathrm{erf}\left(\sqrt{\frac{m}{2\mathrm{i}\hbar t}}(x-x_0)\right) = \Theta(x-x_0) - \Theta(x_0-x).$$

3.11 The initial condition (3.31) yielded a Gaussian wave packet that had its minimal spread in location x exactly at the time $t = 0$. Before that particular moment, the wave packet was contracting and afterwards it was spreading. Find an initial condition $\psi(x, 0)$ for a Gaussian wave packet that will continue to contract for some time Δt before it expands.

Chapter 4

Notions from Linear Algebra and Bra-Ket Notation

The Schrödinger equation (1.14) is linear in the wave function $\psi(\boldsymbol{x}, t)$. This implies that for any set of solutions $\psi_1(\boldsymbol{x}, t)$, $\psi_2(\boldsymbol{x}, t), \ldots$, any linear combination $\psi(\boldsymbol{x}, t) = C_1\psi_1(\boldsymbol{x}, t) + C_2\psi_2(\boldsymbol{x}, t) + \ldots$ with complex coefficients C_n is also a solution. The set of solutions of equation (1.14) for fixed potential V will therefore have the structure of a complex vector space, and we can think of the wave function $\psi(\boldsymbol{x}, t)$ as a particular vector in this vector space. Furthermore, we can map this vector bijectively into different, but equivalent representations where the wave function depends on different variables. An example of this is Fourier transformation (2.5) into a wave function which depends on a wave vector $\boldsymbol{k}$,

$$\psi(\boldsymbol{k}, t) = \frac{1}{\sqrt{2\pi}^3} \int d^3\boldsymbol{x}\, \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\, \psi(\boldsymbol{x}, t).$$

We have already noticed that this is sloppy notation from the mathematical point of view. We should denote the Fourier transformed function with $\tilde{\psi}(\boldsymbol{k}, t)$ to make it clear that $\tilde{\psi}(\boldsymbol{k}, t)$ and $\psi(\boldsymbol{x}, t)$ have different dependencies on their arguments (or stated differently, to make it clear that $\psi(\boldsymbol{k}, t)$ and $\psi(\boldsymbol{x}, t)$ are really different functions). However, there is a reason for the notation in equations (2.4,2.5). We can switch back and forth between $\psi(\boldsymbol{x}, t)$ and $\psi(\boldsymbol{k}, t)$ using Fourier transformation. This implies that any property of a particle that can be calculated from the wave function $\psi(\boldsymbol{x}, t)$ in $\boldsymbol{x}$ space can also be calculated from the wave function $\psi(\boldsymbol{k}, t)$ in $\boldsymbol{k}$ space. Therefore, following Dirac, we nowadays do not think any more of $\psi(\boldsymbol{x}, t)$ as a wave function of a particle, but we rather think more abstractly of $\psi(t)$ as a time-dependent *quantum state*, with particular *representations* of the quantum state $\psi(t)$ given by the wave functions $\psi(\boldsymbol{x}, t)$ or $\psi(\boldsymbol{k}, t)$. There are infinitely more possibilities to represent the quantum state $\psi(t)$ through functions. For example, we could perform a Fourier transformation only with respect to the y variable and represent $\psi(t)$ through the wave function $\psi(x, k_y, z, t)$, or we could perform an invertible transformation to completely different independent variables. In 1939, Paul

R. Dick, *Advanced Quantum Mechanics: Materials and Photons*,
Graduate Texts in Physics, DOI 10.1007/978-1-4419-8077-9_4,
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Dirac introduced a notation in quantum mechanics which emphasizes the vector space and representation aspects of quantum states in a very elegant and suggestive manner. This notation is Dirac's bra-ket notation, and it is ubiquitous in advanced modern quantum mechanics. It is worthwhile to use bra-ket notation from the start, and it is most easily explained in the framework of linear algebra.

4.1 Notions from linear algebra

The mathematical structure of quantum mechanics resembles linear algebra in many respects, and many notions from linear algebra are very useful in the investigation of quantum systems. Bra-ket notation makes the linear algebra aspects of quantum particularly visible and easy to use. Therefore we will first introduce a few notions of linear algebra in standard notation, and then rewrite everything in bra-ket notation.

Tensor products

Suppose $\mathcal{V}$ is an N-dimensional real vector space with a Cartesian basis $\hat{\boldsymbol{e}}_a$, $1 \leq a \leq N$,

$$\hat{\boldsymbol{e}}_a \cdot \hat{\boldsymbol{e}}_b = \delta_{ab}.$$

Furthermore, assume that u^a, v^a are Cartesian components of the two vectors $\boldsymbol{u}$ and $\boldsymbol{v}$,

$$\boldsymbol{u} = \sum_{a=1}^{N} u^a \hat{\boldsymbol{e}}_a \equiv u^a \hat{\boldsymbol{e}}_a.$$

Here we use *summation convention*: Whenever an index appears twice in a multiplicative term, it is automatically summed over its full range of values. We will continue to use this convention throughout the remainder of the book. The *tensor product*

$$\underline{\boldsymbol{M}} = \boldsymbol{u} \otimes \boldsymbol{v}^{\mathrm{T}}$$

of the two vectors is the $N \times N$ matrix with components

$$M^{ab} = u^a v^b$$

in the Cartesian basis. The matrix $\underline{\boldsymbol{M}}$ is called a *2nd rank tensor* due to its transformation properties under linear transformations of the vectors appearing in the product.
Suppose we perform a transformation of the Cartesian basis vectors $\hat{\boldsymbol{e}}_a$ to a new set $\hat{\boldsymbol{e}}'_i$ of basis vectors,

$$\hat{\boldsymbol{e}}_a \to \hat{\boldsymbol{e}}'_i = \hat{\boldsymbol{e}}_a R^a{}_i, \tag{4.1}$$

subject to the constraint that the new basis vectors also provide a Cartesian basis,

$$\hat{\boldsymbol{e}}'_i \cdot \hat{\boldsymbol{e}}'_j = \delta_{ab} R^a{}_i R^b{}_j = R^a{}_i R_{aj} = \delta_{ij}. \tag{4.2}$$

Linear transformations which map Cartesian bases into Cartesian bases are denoted as rotations.
We defined $R_{aj} \equiv \delta_{ab} R^b{}_j$ in equation (4.2), i.e. numerically $R_{aj} = R^a{}_j$. Equation (4.2) is in matrix notation

$$\underline{R}^T \cdot \underline{R} = \underline{1}, \tag{4.3}$$

i.e. $\underline{R}^T = \underline{R}^{-1}$.
However, a change of basis in our vector space does nothing to the vector $\boldsymbol{v}$, except that the vector will have different components with respect to the new basis vectors,

$$\boldsymbol{v} = \hat{\boldsymbol{e}}_a v^a = \hat{\boldsymbol{e}}'_i v'^i = \hat{\boldsymbol{e}}_a R^a{}_i v'^i. \tag{4.4}$$

Equations (4.4) and (4.2) and the uniqueness of the decomposition of a vector with respect to a set of basis vectors imply

$$v^a = R^a{}_i v'^i, \quad v'^i = (R^{-1})^i{}_a v^a = (R^T)^i{}_a v^a = v^a R_a{}^i. \tag{4.5}$$

This is the *passive interpretation* of transformations: The transformation changes the reference frame, but not the physical objects (here: vectors). Therefore the expansion coefficients of the physical objects change inversely (or *contravariant*) to the transformation of the reference frame. We will often use the passive interpretation for symmetry transformations of quantum systems.
The transformation laws (4.1) and (4.5) define *first rank tensors*, because the transformation laws are linear (or first order) in the transformation matrices $\underline{R}$ or $\underline{R}^{-1}$.
The tensor product

$$\underline{\boldsymbol{M}} = \boldsymbol{u} \otimes \boldsymbol{v}^{\mathrm{T}} = u^a v^b \hat{\boldsymbol{e}}_a \otimes \hat{\boldsymbol{e}}_b$$

then defines a *second rank tensor*, because the components and the basis transform quadratically (or in second order) with the transformation matrices $\underline{R}$ or $\underline{R}^{-1}$,

$$M'^{ij} = u'^i v'^j = (R^{-1})^i{}_a (R^{-1})^j{}_b u^a v^b = (R^{-1})^i{}_a (R^{-1})^j{}_b M^{ab}, \tag{4.6}$$

$$\hat{\boldsymbol{e}}'_i \otimes \hat{\boldsymbol{e}}'_j = \hat{\boldsymbol{e}}_a \otimes \hat{\boldsymbol{e}}_b R^a{}_i R^b{}_j. \tag{4.7}$$

The concept immediately generalizes to n-th order tensors.
Writing the tensor product explicitly as $\boldsymbol{u} \otimes \boldsymbol{v}^{\mathrm{T}}$ reminds us that the a-th row of $\underline{\boldsymbol{M}}$ is just the row vector $u^a \boldsymbol{v}^{\mathrm{T}}$, while the b-th column is just the column vector $\boldsymbol{u} v^b$. However, usually one only writes $\boldsymbol{u} \otimes \boldsymbol{v}$ for the tensor product (just as one writes $\boldsymbol{u} \cdot \boldsymbol{v}$ instead of $\boldsymbol{u}^{\mathrm{T}} \cdot \boldsymbol{v}$ for the scalar product).

Dual bases

Now let $\boldsymbol{a}_i$, $1 \leq i \leq N$, be another basis of the vector space $\mathcal{V}$. Generically this basis will not be orthonormal: $\boldsymbol{a}_i \cdot \boldsymbol{a}_j \neq \delta_{ij}$. The corresponding *dual basis* with basis vectors $\boldsymbol{a}^i$ is defined through the requirements

$$\boldsymbol{a}^i \cdot \boldsymbol{a}_j = \delta^i{}_j. \tag{4.8}$$

Apparently a basis is *self-dual* ($\boldsymbol{a}^i = \boldsymbol{a}_i$) if and only if it is orthonormal (i.e. Cartesian).
For the explicit construction of the dual basis, we observe that the scalar product of the N vectors $\boldsymbol{a}_i$ defines a symmetric $N \times N$ matrix

$$g_{ij} = \boldsymbol{a}_i \cdot \boldsymbol{a}_j.$$

This matrix is not degenerate, because otherwise it would have at least one vanishing eigenvalue, i.e. there would exist N numbers X^i (not all vanishing) such that $g_{ij}X^j = 0$. This would imply existence of a non-vanishing vector $\boldsymbol{X} = X^i\boldsymbol{a}_i$ with vanishing length,

$$\boldsymbol{X}^2 = X^iX^j\boldsymbol{a}_i \cdot \boldsymbol{a}_j = X^ig_{ij}X^j = 0.$$

The matrix g_{ij} is therefore invertible, and we denote the inverse matrix with g^{ij},

$$g^{ij}g_{jk} = \delta^i{}_k.$$

The inverse matrix can be used to construct the dual basis vectors as

$$\boldsymbol{a}^i = g^{ij}\boldsymbol{a}_j. \tag{4.9}$$

The condition for dual basis vectors is readily verified,

$$\boldsymbol{a}^i \cdot \boldsymbol{a}_k = g^{ij}\boldsymbol{a}_j \cdot \boldsymbol{a}_k = g^{ij}g_{jk} = \delta^i{}_k.$$

For an example for the construction of a dual basis, consider Figure 4.1. The vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ provide a basis. The angle between $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ is $\pi/4$ radian, and their lengths are $|\boldsymbol{a}_1| = 2$ and $|\boldsymbol{a}_2| = \sqrt{2}$.
The matrix g_{ij} therefore has the following components in this basis,

$$\underline{g} = \begin{pmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{pmatrix} = \begin{pmatrix} \boldsymbol{a}_1 \cdot \boldsymbol{a}_1 & \boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \\ \boldsymbol{a}_2 \cdot \boldsymbol{a}_1 & \boldsymbol{a}_2 \cdot \boldsymbol{a}_2 \end{pmatrix} = \begin{pmatrix} 4 & 2 \\ 2 & 2 \end{pmatrix}.$$

The inverse matrix is then

$$\underline{g}^{-1} = \begin{pmatrix} g^{11} & g^{12} \\ g^{21} & g^{22} \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & -1 \\ -1 & 2 \end{pmatrix}.$$

This yields with (4.9) the dual basis vectors

$$\boldsymbol{a}^1 = \frac{1}{2}\boldsymbol{a}_1 - \frac{1}{2}\boldsymbol{a}_2, \quad \boldsymbol{a}^2 = -\frac{1}{2}\boldsymbol{a}_1 + \boldsymbol{a}_2.$$

These equations determined the vectors $\boldsymbol{a}^i$ in Figure 4.1.

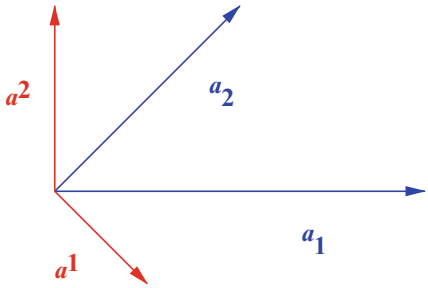


Figure 4.1: The blue vectors are the basis vectors $\boldsymbol{a}_i$. The red vectors are the dual basis vectors $\boldsymbol{a}^i$.

Decomposition of the identity

Equation (4.8) implies that the decomposition of a vector $\boldsymbol{v} \in \mathcal{V}$ with respect to the basis $\boldsymbol{a}_i$ can be written as (note summation convention)

$$\boldsymbol{v} = \boldsymbol{a}_i(\boldsymbol{a}^i \cdot \boldsymbol{v}), \tag{4.10}$$

i.e. the projection of $\boldsymbol{v}$ onto the i-th basis vector $\boldsymbol{a}_i$ (the component v^i in standard notation) is given through scalar multiplication with the dual basis vector $\boldsymbol{a}^i$:

$$v^i = \boldsymbol{a}^i \cdot \boldsymbol{v}.$$

The right hand side of equation (4.10) contains three vectors in each summand, and brackets have been employed to emphasize that the scalar product is between the two rightmost vectors in each term. Another way to make that clear is to write the combination of the two leftmost vectors in each term as a tensor product:

$$\boldsymbol{v} = \boldsymbol{a}_i \otimes \boldsymbol{a}^i \cdot \boldsymbol{v}.$$

If we first evaluate all the tensor products and sum over i, we have for every vector $\boldsymbol{v} \in \mathcal{V}$

$$\boldsymbol{v} = (\boldsymbol{a}_i \otimes \boldsymbol{a}^i) \cdot \boldsymbol{v},$$

which makes it clear that the sum of tensor products in this equation adds up to the identity matrix,

$$\boldsymbol{a}_i \otimes \boldsymbol{a}^i = \underline{1}. \tag{4.11}$$

This is the statement that every vector can be uniquely decomposed in terms of the basis $\boldsymbol{a}_i$, and therefore this is a basic example of a *completeness relation*.

Note that we can just as well expand $\boldsymbol{v}$ with respect to the dual basis:

$$\boldsymbol{v} = v_i \boldsymbol{a}^i = \boldsymbol{a}^i (\boldsymbol{a}_i \cdot \boldsymbol{v}) = (\boldsymbol{a}^i \otimes \boldsymbol{a}_i) \cdot \boldsymbol{v},$$

and therefore we also have the dual completeness relation

$$\boldsymbol{a}^i \otimes \boldsymbol{a}_i = \underline{1}.$$

We could also have inferred this from transposition of equation (4.11).
Linear transformations of vectors can be written in terms of matrices,

$$\boldsymbol{v}' = \underline{\boldsymbol{A}} \cdot \boldsymbol{v}.$$

If we insert the decompositions with respect to the basis $\boldsymbol{a}_i$,

$$\boldsymbol{v}' = \boldsymbol{a}_i \otimes \boldsymbol{a}^i \cdot \boldsymbol{v}' = \boldsymbol{a}_i \otimes \boldsymbol{a}^i \cdot \underline{\boldsymbol{A}} \cdot \boldsymbol{a}_j \otimes \boldsymbol{a}^j \cdot \boldsymbol{v},$$

we find the equation in components $v'^i = A^i{}_j v^j$, with the matrix elements of the operator A,

$$A^i{}_j = \boldsymbol{a}^i \cdot \underline{\boldsymbol{A}} \cdot \boldsymbol{a}_j.$$

An application of dual bases in solid state physics: The Laue conditions for elastic scattering off a crystal

Non-orthonormal bases and the corresponding dual bases play an important role in solid state physics. Assume e.g. that $\boldsymbol{a}_i$, $1 \leq i \leq 3$, are the three fundamental translation vectors of a three-dimensional lattice L. They generate the lattice according to

$$\boldsymbol{\ell} = \boldsymbol{a}_i m^i, \quad m^i \in \mathbb{Z}.$$

In three dimensions one can easily construct the dual basis vectors using cross products:

$$\boldsymbol{a}^i = \epsilon^{ijk} \frac{\boldsymbol{a}_j \times \boldsymbol{a}_k}{2\boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)} = \frac{1}{2V} \epsilon^{ijk} \boldsymbol{a}_j \times \boldsymbol{a}_k, \tag{4.12}$$

where $V = \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)$ is the volume of the lattice cell spanned by the basis vectors $\boldsymbol{a}_i$.
The vectors $\boldsymbol{a}^i$, $1 \leq i \leq 3$, generate the *dual lattice* or *reciprocal lattice* $\tilde{L}$ according to

$$\tilde{\boldsymbol{\ell}} = n_i \boldsymbol{a}^i, \quad n_i \in \mathbb{Z},$$

and the volume of a cell in the dual lattice is

$$\tilde{V} = \boldsymbol{a}^1 \cdot (\boldsymbol{a}^2 \times \boldsymbol{a}^3) = \frac{1}{V}. \tag{4.13}$$

Max von Laue derived in 1912 the conditions for constructive interference in the coherent elastic scattering off a regular array of scattering centers. If the directions of the incident and scattered waves of wavelength λ are $\hat{\boldsymbol{e}}_{\boldsymbol{k}}$ and $\hat{\boldsymbol{e}}'_{\boldsymbol{k}}$, as shown in Figure 4.2, the condition for constructive interference from all scattering centers along a line generated by $\boldsymbol{a}_i$ is

$$|\boldsymbol{a}_i|\,(\cos\alpha' - \cos\alpha) = (\hat{\boldsymbol{e}}'_{\boldsymbol{k}} - \hat{\boldsymbol{e}}_{\boldsymbol{k}}) \cdot \boldsymbol{a}_i = n_i\lambda, \tag{4.14}$$

with integer numbers n_i.

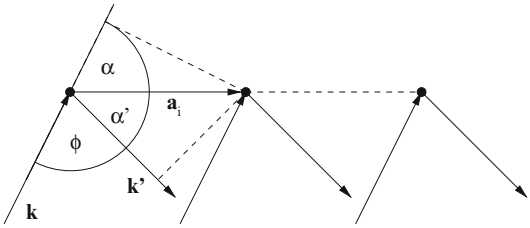


Figure 4.2: The Laue equation (4.14) is the condition for constructive interference between scattering centers along the line generated by the primitive basis vector $\boldsymbol{a}_i$.

In terms of the wavevector shift

$$\Delta\boldsymbol{k} = \boldsymbol{k}' - \boldsymbol{k} = \frac{2\pi}{\lambda}\,(\hat{\boldsymbol{e}}'_{\boldsymbol{k}} - \hat{\boldsymbol{e}}_{\boldsymbol{k}})$$

equation (4.14) can be written more neatly as

$$\Delta\boldsymbol{k} \cdot \boldsymbol{a}_i = 2\pi n_i. \tag{4.15}$$

If we want to have constructive interference from all scattering centers in the crystal this condition must hold for all three values of i. In case of surface scattering equation (4.15) must only hold for the two vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ which generate the lattice structure of the scattering centers on the surface.
In 1913 W.L. Bragg observed that for scattering from a bulk crystal equations (4.15) are equivalent to constructive interference from specular reflection from sets of equidistant parallel planes in the crystal, and that the Laue conditions can be reduced to the Bragg equation in this case. However, for scattering from one or two-dimensional crystals[1] and for the Ewald construction one still has to use the Laue conditions.

[1]For scattering off two-dimensional crystals the Laue conditions can be recast in simpler forms in special cases. E.g. for orthogonal incidence a plane grating equation can be derived from the Laue conditions, or if the momentum transfer $\Delta\boldsymbol{k}$ is in the plane of the crystal a two-dimensional Bragg equation can be derived.

If we study scattering off a three-dimensional crystal, we know that the three dual basis vectors $\boldsymbol{a}^i$ span the whole three-dimensional space. Like any three-dimensional vector, the wavevector shift can then be expanded in terms of the dual basis vectors according to

$$\Delta\boldsymbol{k} = \boldsymbol{a}^i(\boldsymbol{a}_i \cdot \Delta\boldsymbol{k}),$$

and substitution of equation (4.15) yields

$$\Delta\boldsymbol{k} = 2\pi n_i \boldsymbol{a}^i,$$

i.e. the condition for constructive interference from coherent elastic scattering off a three-dimensional crystal is equivalent to the statement that $\Delta\boldsymbol{k}/(2\pi)$ is a vector in the dual lattice $\tilde{L}$. Furthermore, energy conservation in the elastic scattering implies $|\boldsymbol{p}'| = |\boldsymbol{p}|$,

$$\Delta\boldsymbol{k}^2 + 2\boldsymbol{k} \cdot \Delta\boldsymbol{k} = 0. \tag{4.16}$$

Equations (4.15) and (4.16) together lead to the Ewald construction for the momenta of elastically scattered beams (see Figure 4.3): Draw the dual lattice and multiply all distances by a factor 2π. Then draw the vector $-\boldsymbol{k}$ from one (arbitrary) point of this rescaled dual lattice. Draw a sphere of radius $|\boldsymbol{k}|$ around the endpoint of $-\boldsymbol{k}$. Any point in the rescaled dual lattice which lies on this sphere corresponds to the $\boldsymbol{k}'$ vector of an elastically scattered beam; $\boldsymbol{k}'$ points from the endpoint of $-\boldsymbol{k}$ (the center of the sphere) to the rescaled dual lattice point on the sphere.

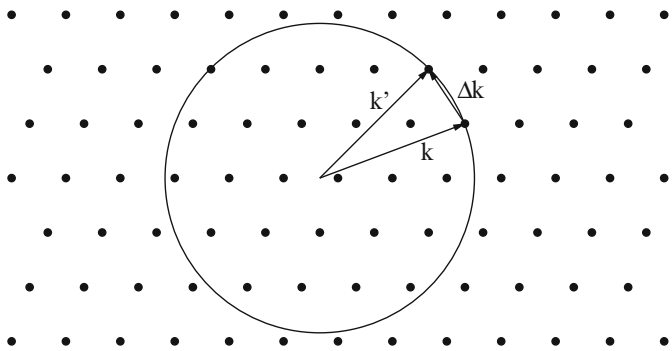


Figure 4.3: The Ewald construction of the wave vectors of elastically scattered beams. The points correspond to the reciprocal lattice stretched with the factor 2π.

We have already noticed that for scattering off a planar array of scattering centers, equation (4.15) must only hold for the two vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ which generate the lattice structure of the scattering centers on the surface. And if

we have only a linear array of scattering centers, equation (4.15) must only hold for the vector $\boldsymbol{a}_1$ which generates the linear array. In those two cases the wavevector shift can be decomposed into components orthogonal and parallel to the scattering surface or line, and the Laue conditions then imply that the parallel component is a vector in the rescaled dual lattice,

$$\Delta\boldsymbol{k} = \Delta\boldsymbol{k}_\perp + \Delta\boldsymbol{k}_\parallel = \Delta\boldsymbol{k}_\perp + \boldsymbol{a}^i(\boldsymbol{a}_i \cdot \Delta\boldsymbol{k}) = \Delta\boldsymbol{k}_\perp + 2\pi n_i \boldsymbol{a}^i.$$

The rescaled dual lattice is also important in the *umklapp* processes in phonon-phonon or electron-phonon scattering in crystals. Lattices can only support oscillations with wavelengths larger than certain minimal wavelengths, which are determined by the crystal structure. As a result momentum conservation in phonon-phonon or electron-phonon scattering involves the rescaled dual lattice,

$$\sum \boldsymbol{k}_{in} - \sum \boldsymbol{k}_{out} \in 2\pi \times \tilde{L},$$

see textbooks on solid state physics.

Bra-ket notation in linear algebra

The translation of the previous notions in linear algebra into bra-ket notation starts with the notion of a *ket vector* for a vector, $\boldsymbol{v} = |v\rangle$, and a *bra vector* for a transposed vector, $\boldsymbol{v}^{\mathrm{T}} = \langle v|$. The tensor product is

$$\boldsymbol{u} \otimes \boldsymbol{v}^{\mathrm{T}} = |u\rangle\langle v|,$$

and the scalar product is

$$\boldsymbol{u}^{\mathrm{T}} \cdot \boldsymbol{v} = \langle u|v\rangle.$$

The appearance of the brackets on the right hand side motivated the designation bra vector for a transposed vector and ket vector for a vector.
The decomposition of a vector in the basis $|a_i\rangle$, using the dual basis $|a^i\rangle$ is

$$|v\rangle = |a_i\rangle\langle a^i|v\rangle,$$

and corresponds to the decomposition of the identity

$$|a_i\rangle\langle a^i| = \underline{1}.$$

A linear operator maps vectors $|v\rangle$ into vectors $|v'\rangle$, $|v'\rangle = A|v\rangle$. This reads in components

$$\langle a^i|v'\rangle = \langle a^i|A|v\rangle = \langle a^i|A|a_j\rangle\langle a^j|v\rangle,$$

where

$$A^i{}_j \equiv \langle a^i|A|a_j\rangle$$

are the matrix elements of the linear operator A. There is no real advantage in using bra-ket notation in the linear algebra of finite-dimensional vector spaces, but it turns out to be very useful in quantum mechanics.

4.2 Bra-ket notation in quantum mechanics

We can represent a state as a probability amplitude in $\boldsymbol{x}$-space or in $\boldsymbol{k}$-space, and we can switch between both representations through Fourier transformation. The state itself is apparently independent from which representation we choose, just like a vector is independent from the particular basis in which we expand the vector. In Chapter 7 we will derive a wave function $\psi_{1s}(\boldsymbol{x}, t)$ for the relative motion of the proton and the electron in the lowest energy state of a hydrogen atom. However, it does not matter whether we use the wave function $\psi_{1s}(\boldsymbol{x}, t)$ in $\boldsymbol{x}$-space or the Fourier transformed wave function $\psi_{1s}(\boldsymbol{k}, t)$ in $\boldsymbol{k}$-space to calculate observables for the ground state of the hydrogen atom. Every information on the state can be retrieved from each of the two wave functions. We can also contemplate more exotic possibilities like writing the ψ_{1s} state as a linear combination of the oscillator eigenstates that we will encounter in Chapter 6. There are infinitely many possibilities to write down wave functions for one and the same quantum state, and all possibilities are equivalent. Therefore wave functions are only particular representations of a state, just like the components $\langle a^i|v\rangle$ of a vector $|v\rangle$ in an N-dimensional vector space provide only a representation of the vector with respect to a particular basis $|a_i\rangle$, $1 \leq i \leq N$.
This motivates the following adaptation of bra-ket notation: The (generically time-dependent) state of a quantum system is $|\psi(t)\rangle$, and the $\boldsymbol{x}$-representation is just the specification of $|\psi(t)\rangle$ in terms of its projection on a particular basis,

$$\psi(\boldsymbol{x}, t) = \langle \boldsymbol{x}|\psi(t)\rangle,$$

where the "basis" is given by the non-enumerable set of "$\mathbf{x}$-eigenkets":

$$\mathbf{x}|\boldsymbol{x}\rangle = \boldsymbol{x}|\boldsymbol{x}\rangle. \tag{4.17}$$

Here $\mathbf{x}$ is the operator, or rather a vector of operators $\mathbf{x} = (\mathrm{x}, \mathrm{y}, \mathrm{z})$, and $\boldsymbol{x} = (x, y, z)$ is the corresponding vector of eigenvalues.
In advanced quantum mechanics, the operators for location or momentum of a particle and their eigenvalues are sometimes not explicitly distinguished in notation, but for the experienced reader it is always clear from the context whether e.g. $\boldsymbol{x}$ refers to the operator or the eigenvalue. We will denote the operators $\mathbf{x}$ and $\mathbf{p}$ for location and momentum and their Cartesian components with upright notation, $\mathbf{x} = (\mathrm{x}, \mathrm{y}, \mathrm{z})$, $\mathbf{p} = (\mathrm{p}_x, \mathrm{p}_y, \mathrm{p}_z)$, while their eigenvalue vectors and Cartesian eigenvalues are written in cursive notation, $\boldsymbol{x} = (x, y, z)$ and $\boldsymbol{p} = \hbar\boldsymbol{k} = (p_x, p_y, p_z)$. However, this becomes very clumsy for non-Cartesian components of the operators $\mathbf{x}$ and $\mathbf{p}$, but once we are at the stage where we have to use e.g. both location operators and their eigenvalues in polar coordinates, you will have so much practice with bra-ket notation that you will infer from the context whether e.g. r refers to the operator $r = \sqrt{\mathrm{x}^2 + \mathrm{y}^2 + \mathrm{z}^2}$ or to the eigenvalue $r = \sqrt{x^2 + y^2 + z^2}$. Some physical quantities have different symbols for the related operator and its eigenvalues, e.g. H for the energy

operator and E for its eigenvalues,

$$H|E\rangle = E|E\rangle,$$

so that in these cases the use of standard cursive mathematical notation for the operators and the eigenvalues cannot cause confusion.
The "momentum-eigenkets" provide another basis of quantum states of a particle,

$$\mathbf{p}|\boldsymbol{k}\rangle = \hbar\boldsymbol{k}|\boldsymbol{k}\rangle, \tag{4.18}$$

and the change of basis looks like the corresponding equation in linear algebra: If we have two sets of basis vectors $|a_i\rangle$, $|b_a\rangle$, then the components of a vector $|v\rangle$ with respect to the new basis $|b_a\rangle$ are related to the $|a_i\rangle$-components via (just insert $|v\rangle = |a_i\rangle\langle a^i|v\rangle$)

$$\langle b^a|v\rangle = \langle b^a|a_i\rangle\langle a^i|v\rangle,$$

i.e. the transformation matrix $T^a{}_i = \langle b^a|a_i\rangle$ is just given by the components of the old basis vectors in the new basis.
The corresponding equation in quantum mechanics for the $|\boldsymbol{x}\rangle$ and $|\boldsymbol{k}\rangle$ bases is

$$\langle \boldsymbol{x}|\psi(t)\rangle = \int d^3\boldsymbol{k}\,\langle \boldsymbol{x}|\boldsymbol{k}\rangle\langle \boldsymbol{k}|\psi(t)\rangle = \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\,\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\langle \boldsymbol{k}|\psi(t)\rangle,$$

which tells us that the expansion coefficients of the vectors $|\boldsymbol{k}\rangle$ with respect to the $|\boldsymbol{x}\rangle$-basis are just

$$\langle \boldsymbol{x}|\boldsymbol{k}\rangle = \frac{1}{\sqrt{2\pi}^3}\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}). \tag{4.19}$$

The Fourier decomposition of the δ-function implies that these bases are self-dual, e.g.

$$\langle \boldsymbol{x}|\boldsymbol{x}'\rangle = \int d^3\boldsymbol{k}\,\langle \boldsymbol{x}|\boldsymbol{k}\rangle\langle \boldsymbol{k}|\boldsymbol{x}'\rangle = \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\,\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')] = \delta(\boldsymbol{x}-\boldsymbol{x}').$$

The scalar product of two states can be written in terms of $|\boldsymbol{x}\rangle$-components or $|\boldsymbol{k}\rangle$-components

$$\begin{aligned}\langle\varphi(t)|\psi(t)\rangle &= \int d^3\boldsymbol{x}\,\langle\varphi(t)|\boldsymbol{x}\rangle\langle\boldsymbol{x}|\psi(t)\rangle = \int d^3\boldsymbol{x}\,\varphi^+(\boldsymbol{x},t)\psi(\boldsymbol{x},t)\\ &= \int d^3\boldsymbol{x}\,\langle\varphi(t)|\boldsymbol{k}\rangle\langle\boldsymbol{k}|\psi(t)\rangle = \int d^3\boldsymbol{x}\,\varphi^+(\boldsymbol{k},t)\psi(\boldsymbol{k},t).\end{aligned}$$

To get some practice with bra-ket notation let us derive the $\boldsymbol{x}$-representation of the momentum operator. We know equation (4.18) and we want to find out

what the $\boldsymbol{x}$-components of the state $\boldsymbol{p}|\psi(t)\rangle$ are. We can accomplish this by inserting the decomposition

$$|\psi(t)\rangle = \int d^3\boldsymbol{k}\, |\boldsymbol{k}\rangle\langle\boldsymbol{k}|\psi(t)\rangle$$

into $\langle\boldsymbol{x}|\mathbf{p}|\psi(t)\rangle$,

$$\langle\boldsymbol{x}|\mathbf{p}|\psi(t)\rangle = \int d^3\boldsymbol{k}\, \langle\boldsymbol{x}|\mathbf{p}|\boldsymbol{k}\rangle\langle\boldsymbol{k}|\psi(t)\rangle = \int d^3\boldsymbol{k}\, \hbar\boldsymbol{k}\langle\boldsymbol{x}|\boldsymbol{k}\rangle\langle\boldsymbol{k}|\psi(t)\rangle. \tag{4.20}$$

However, equation (4.19) implies

$$\hbar\boldsymbol{k}\langle\boldsymbol{x}|\boldsymbol{k}\rangle = \frac{\hbar}{\mathrm{i}}\boldsymbol{\nabla}\langle\boldsymbol{x}|\boldsymbol{k}\rangle,$$

and substitution into equation (4.20) yields

$$\langle\boldsymbol{x}|\mathbf{p}|\psi(t)\rangle = \frac{\hbar}{\mathrm{i}}\boldsymbol{\nabla}\int d^3\boldsymbol{k}\, \langle\boldsymbol{x}|\boldsymbol{k}\rangle\langle\boldsymbol{k}|\psi(t)\rangle = \frac{\hbar}{\mathrm{i}}\boldsymbol{\nabla}\langle\boldsymbol{x}|\psi(t)\rangle. \tag{4.21}$$

This equation yields in particular the matrix elements of the momentum operator in the $|\boldsymbol{x}\rangle$-basis,

$$\langle\boldsymbol{x}|\mathbf{p}|\boldsymbol{x}'\rangle = \frac{\hbar}{\mathrm{i}}\boldsymbol{\nabla}\delta(\boldsymbol{x}-\boldsymbol{x}').$$

Equation (4.21) means that the $\boldsymbol{x}$-expansion coefficients $\langle\boldsymbol{x}|\mathbf{p}|\psi(t)\rangle$ of the new state $\mathbf{p}|\psi(t)\rangle$ can be calculated from the expansion coefficients $\langle\boldsymbol{x}|\psi(t)\rangle$ of the old state $|\psi(t)\rangle$ through application of $-\mathrm{i}\hbar\boldsymbol{\nabla}$. In sloppy terminology this is the statement "the $\boldsymbol{x}$-representation of the momentum operator is $-\mathrm{i}\hbar\boldsymbol{\nabla}$", but the proper statement is equation (4.21),

$$\langle\boldsymbol{x}|\mathbf{p}|\psi(t)\rangle = \frac{\hbar}{\mathrm{i}}\boldsymbol{\nabla}\langle\boldsymbol{x}|\psi(t)\rangle.$$

The quantum operator $\mathbf{p}$ acts on the quantum state $|\psi(t)\rangle$, the differential operator $-\mathrm{i}\hbar\boldsymbol{\nabla}$ acts on the expansion coefficients $\langle\boldsymbol{x}|\psi(t)\rangle$ of the state $|\psi(t)\rangle$. The corresponding statement in linear algebra is that a linear transformation A transforms a vector $|v\rangle$ according to

$$|v\rangle \;\rightarrow\; |v'\rangle = A|v\rangle,$$

and the transformation in a particular basis reads

$$\langle a^i|v'\rangle = \langle a^i|A|v\rangle = \langle a^i|A|a_j\rangle\langle a^j|v\rangle.$$

The operator A acts on the vector, and its representation $\langle a^i|A|a_j\rangle$ in a particular basis acts on the components of the vector in that basis.
Bra-ket notation requires a proper understanding of the distinction between quantum operators (like $\mathbf{p}$) and operators that act on expansion coefficients of

quantum states in a particular basis (like $-\mathrm{i}\hbar\boldsymbol{\nabla}$). Bra-ket notation appears in virtually every equation of advanced quantum mechanics and quantum field theory. It provides in many respects the most useful notation for recognizing the elegance and power of quantum theory.
Equations equivalent to equations (4.17,4.18,4.21) are contained in

$$\mathbf{x} = \int d^3\boldsymbol{x}\, |\boldsymbol{x}\rangle\boldsymbol{x}\langle\boldsymbol{x}| = \int d^3\boldsymbol{k}\, |\boldsymbol{k}\rangle \mathrm{i}\frac{\partial}{\partial \boldsymbol{k}}\langle\boldsymbol{k}|, \tag{4.22}$$

$$\mathbf{p} = \int d^3\boldsymbol{k}\, |\boldsymbol{k}\rangle\hbar\boldsymbol{k}\langle\boldsymbol{k}| = \int d^3\boldsymbol{x}\, |\boldsymbol{x}\rangle \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \boldsymbol{x}}\langle\boldsymbol{x}|. \tag{4.23}$$

Here we used the very convenient notation $\boldsymbol{\nabla} \equiv \partial/\partial\boldsymbol{x}$ for the del operator in $\boldsymbol{x}$ space, and $\partial/\partial\boldsymbol{k}$ for the del operator in $\boldsymbol{k}$ space. One often encounters several copies of several vector spaces in an equation, and this notation is extremely useful to distinguish the different del operators in the different vector spaces.
Functions of operators are operators again. An important example are the operators $V(\mathbf{x})$ for the potential energy of a particle. The eigenkets of $\mathbf{x}$ are also eigenkets of $V(\mathbf{x})$,

$$V(\mathbf{x})|\boldsymbol{x}\rangle = V(\boldsymbol{x})|\boldsymbol{x}\rangle,$$

and the matrix elements in $\boldsymbol{x}$ representation are

$$\langle\boldsymbol{x}|V(\mathbf{x})|\boldsymbol{x}'\rangle = V(\boldsymbol{x}')\delta(\boldsymbol{x}-\boldsymbol{x}').$$

The single particle Schrödinger equation (1.14) is in representation free notation

$$\mathrm{i}\hbar\frac{d}{dt}|\psi(t)\rangle = H|\psi(t)\rangle = \frac{\mathbf{p}^2}{2m}|\psi(t)\rangle + V(\mathbf{x})|\psi(t)\rangle. \tag{4.24}$$

We recover the $\boldsymbol{x}$ representation already used in (1.14) through projection on $\langle\boldsymbol{x}|$ and substitution of

$$1 = \int d^3\boldsymbol{x}'\, |\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|,$$

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\langle\boldsymbol{x}|\psi(t)\rangle = -\frac{\hbar^2}{2m}\Delta\langle\boldsymbol{x}|\psi(t)\rangle + V(\boldsymbol{x})\langle\boldsymbol{x}|\psi(t)\rangle.$$

The definition of adjoint operators in representation-free bra-ket notation is

$$\langle\varphi|A|\psi\rangle = \langle\psi|A^+|\varphi\rangle^+. \tag{4.25}$$

Self-adjoint operators (e.g. $p^+ = p$) have real expectation values and in particular real eigenvalues:

$$\langle\psi|\mathrm{p}|\psi\rangle = \langle\psi|\mathrm{p}^+|\psi\rangle^+ = \langle\psi|\mathrm{p}|\psi\rangle^+.$$

Observables are therefore described by self-adjoint operators in quantum mechanics.

Unitary operators ($U^+ = U^{-1}$) do not change the norm of a state: Substitution of $|\psi\rangle = U|\varphi\rangle$ into $\langle\psi|\psi\rangle$ yields

$$\langle\psi|\psi\rangle = \langle\psi|U|\varphi\rangle = \langle\varphi|U^+|\psi\rangle^+ = \langle\varphi|U^+U|\varphi\rangle^+ = \langle\varphi|\varphi\rangle^+ = \langle\varphi|\varphi\rangle.$$

Time evolution and symmetry transformations of quantum systems are described by unitary operators.

4.3 The adjoint Schrödinger equation and the virial theorem

We consider a matrix element

$$\langle\psi(t)|A(t')|\phi(t')\rangle = (\langle\phi(t')|A^+(t')|\psi(t)\rangle)^+. \tag{4.26}$$

We assume that $|\psi(t)\rangle$ satisfies the Schrödinger equation

$$\mathrm{i}\hbar\frac{d}{dt}|\psi(t)\rangle = H|\psi(t)\rangle,$$

while $A(t')$ and $|\phi(t')\rangle$ are an arbitrary operator and state, respectively. We have artificially taken the state $|\Phi(t')\rangle = A(t')|\phi(t')\rangle$ at another time t', because we are particularly interested in the time-dependence of the matrix element $\langle\psi(t)|A(t')|\phi(t')\rangle$ which arises from the time-dependence of $|\psi(t)\rangle$. Equation (4.26), the Schrödinger equation, and hermiticity of H imply

$$\begin{aligned}\frac{d}{dt}\langle\psi(t)|A(t')|\phi(t')\rangle &= \left(\langle\phi(t')|A^+(t')\frac{d}{dt}|\psi(t)\rangle\right)^+ \\ &= \left(\frac{1}{\mathrm{i}\hbar}\langle\phi(t')|A^+(t')H|\psi(t)\rangle\right)^+ \\ &= \frac{\mathrm{i}}{\hbar}\langle\psi(t)|HA(t')|\phi(t')\rangle.\end{aligned}$$

Since this holds for every operator $A(t')$ and state $|\phi(t')\rangle$, we have an operator equation

$$\left(\frac{d}{dt}\langle\psi(t)|\right) = \frac{\mathrm{i}}{\hbar}\langle\psi(t)|H. \tag{4.27}$$

With the brackets on the left hand side, this equation also holds for projection on time-dependent states of the form $A(t)|\phi(t)\rangle$: Projection of any state $|\Phi(t)\rangle$ on $(d\langle\psi(t)|/dt)$ is equivalent to action of H on $|\Phi(t)\rangle$ followed by projection of $H|\Phi(t)\rangle$ on $(\mathrm{i}/\hbar)\langle\psi(t)|$,

$$\begin{aligned}\frac{d}{dt}\langle\psi(t)|A(t)|\phi(t)\rangle = \frac{\mathrm{i}}{\hbar}\langle\psi(t)|HA(t)|\phi(t)\rangle + \langle\psi(t)|\frac{dA(t)}{dt}|\phi(t)\rangle \\ + \langle\psi(t)|A(t)\frac{d}{dt}|\phi(t)\rangle.\end{aligned}$$

In particular, if $|\phi(t)\rangle$ also satisfies the Schrödinger equation, we have

$$\frac{d}{dt}\langle\psi(t)|A(t)|\phi(t)\rangle = \frac{\mathrm{i}}{\hbar}\langle\psi(t)|[H,A(t)]|\phi(t)\rangle + \langle\psi(t)|\frac{dA(t)}{dt}|\phi(t)\rangle. \tag{4.28}$$

The operator equation (4.27) is the adjoint Schrödinger equation. In general it is an operator equation, but it reduces to the complex conjugate of the Schrödinger equation if it is projected onto $\mathbf{x}$ eigenkets,

$$\begin{aligned}\frac{d}{dt}\langle\psi(t)|\boldsymbol{x}\rangle &= \frac{\mathrm{i}}{\hbar}\int d^3\boldsymbol{x}'\,\langle\psi(t)|\boldsymbol{x}'\rangle\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\boldsymbol{x}'^2}+V(\boldsymbol{x}')\right)\delta(\boldsymbol{x}'-\boldsymbol{x})\\ &= \frac{\mathrm{i}}{\hbar}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\boldsymbol{x}^2}+V(\boldsymbol{x})\right)\langle\psi(t)|\boldsymbol{x}\rangle.\end{aligned}$$

The result (4.28) for the time-dependence of matrix elements appears in many different settings in quantum mechanics, but one application that we will address now concerns the particular choice of the virial operator $\mathbf{x}\cdot\mathbf{p}$ for the operator A. In classical mechanics, Newton's equation and $m\dot{\boldsymbol{x}} = \boldsymbol{p}$ imply that the time derivative of the virial $\boldsymbol{x}\cdot\boldsymbol{p}$ is

$$\frac{d}{dt}\boldsymbol{x}\cdot\boldsymbol{p} = \frac{\boldsymbol{p}^2}{m} - \boldsymbol{x}\cdot\boldsymbol{\nabla}V(\boldsymbol{x}).$$

Application of the time averaging operation $\lim_{T\to\infty}\int_0^T dt\ldots$ on both sides of this equation then yields the classical virial theorem for the time average $\langle K\rangle_T$ of the kinetic energy $K = \boldsymbol{p}^2/2m$,

$$2\langle K\rangle_T = \langle\boldsymbol{x}\cdot\boldsymbol{\nabla}V(\boldsymbol{x})\rangle_T. \tag{4.29}$$

The equation (4.28) applied to $A = \mathbf{x}\cdot\mathbf{p}$ implies that the same relation holds for all matrix elements of the operators $K = \mathbf{p}^2/2m$ and $\mathbf{x}\cdot\boldsymbol{\nabla}V(\mathbf{x})$. We have

$$\frac{\mathrm{i}}{\hbar}[H,\mathbf{x}\cdot\mathbf{p}] = \frac{\mathbf{p}^2}{m} - \mathbf{x}\cdot\frac{\partial}{\partial\mathbf{x}}V(\mathbf{x}),$$

and therefore

$$\frac{d}{dt}\langle\psi(t)|\mathbf{x}\cdot\mathbf{p}|\phi(t)\rangle = 2\langle\psi(t)|K|\phi(t)\rangle - \langle\psi(t)|\mathbf{x}\cdot\frac{\partial}{\partial\mathbf{x}}V(\mathbf{x})|\phi(t)\rangle. \tag{4.30}$$

Time averaging then yields a quantum analog of the classical virial theorem,

$$2\langle\psi(t)|K|\phi(t)\rangle_T = \langle\psi(t)|\mathbf{x}\cdot\frac{\partial}{\partial\mathbf{x}}V(\mathbf{x})|\phi(t)\rangle_T. \tag{4.31}$$

However, if $|\psi(t)\rangle$ and $|\phi(t)\rangle$ are energy eigenstates,

$$|\psi(t)\rangle = |\psi\rangle\exp(-\mathrm{i}E_\psi t/\hbar), \quad |\phi(t)\rangle = |\phi\rangle\exp(-\mathrm{i}E_\phi t/\hbar),$$

then equation (4.30) yields

$$\frac{\mathrm{i}}{\hbar}(E_\psi - E_\phi)\langle\psi|\mathbf{x}\cdot\mathbf{p}|\phi\rangle = 2\langle\psi|K|\phi\rangle - \langle\psi|\mathbf{x}\cdot\frac{\partial}{\partial\mathbf{x}}V(\mathbf{x})|\phi\rangle. \tag{4.32}$$

In this case, the classical time averaging cannot yield anything interesting, but if we assume that our energy eigenstates are degenerate normalizable states,

$$E_\psi = E_\phi, \quad \langle\psi|\psi\rangle = \langle\phi|\phi\rangle = 1,$$

then we find the quantum virial theorem for matrix elements of degenerate normalizable energy eigenstates[2],

$$2\langle\psi|K|\phi\rangle = \langle\psi|\mathbf{x}\cdot\frac{\partial}{\partial\mathbf{x}}V(\mathbf{x})|\phi\rangle. \tag{4.33}$$

Furthermore, if $V(\boldsymbol{x})$ is homogeneous of order ν,

$$V(a\boldsymbol{x}) = a^\nu V(\boldsymbol{x}),$$

then

$$\boldsymbol{x}\cdot\boldsymbol{\nabla}V(\boldsymbol{x}) = \nu V(\boldsymbol{x})$$

and

$$2\langle\psi|K|\phi\rangle = \nu\langle\psi|V|\phi\rangle. \tag{4.34}$$

The relations (4.33) and (4.34) hold in particular for the expectation values of normalizable energy eigenstates. Special cases for the appearance of physically relevant homogeneous potential functions include harmonic oscillators, $\nu = 2$, and the three-dimensional Coulomb potential, $\nu = -1$. We will discuss harmonic oscillators and the Coulomb problem in Chapters 6 and 7, respectively. Equation (4.34) has also profound implications for hypothetical physics in higher dimensions, see Problem 5 in Chapter 20.

4.4 Problems

4.1 We consider again the rotation (4.1) of a Cartesian basis,

$$\hat{\boldsymbol{e}}_a \to \hat{\boldsymbol{e}}'_i = \hat{\boldsymbol{e}}_a R^a{}_i,$$

but this time we insist on keeping the expansion coefficients v^a of the vector $\boldsymbol{v} = v^a\hat{\boldsymbol{e}}_a$. Rotation of the basis with fixed expansion coefficents $\{v^1, \ldots v^N\}$ will therefore generate a new vector

$$\boldsymbol{v} \to \boldsymbol{v}' \equiv v^i\hat{\boldsymbol{e}}'_i.$$

This is the *active interpretation* of transformations, because the change of the reference frame is accompanied by a change of the physical objects.

[2]Normalizability is important for the correctness of equation (4.33), because for states in an energy continuum the left hand side of equation (4.32) may not vanish in the degenerate limit $E_\psi \to E_\phi$, see Problem 8.

In the active interpretation, transformations of the expansion coefficients are defined by the condition that the transformed expansion coefficients describe the expansion of the *new* vector $\boldsymbol{v}'$ with respect to the *old* basis $\hat{\boldsymbol{e}}_a$,

$$\boldsymbol{v}' \equiv v^i \hat{\boldsymbol{e}}'_i = v'^a \hat{\boldsymbol{e}}_a. \tag{4.35}$$

How are the new expansion coefficients v'^a related to the old expansion coefficients v^i for an active transformation?
In the active interpretation, rotations are special by preserving the lengths of vectors and the angles between vectors.
Equation (4.35) implies that we can describe an active transformation either through a transformation of the basis with fixed expansion coefficients, or equivalently through a transformation of the expansion coefficients with a fixed basis. This is very different from the passive transformation, where a transformation of the basis is always accompanied by a compensating contragredient transformation of the expansion coefficients.

4.2 Two basis vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ have length one and the angle between the vectors is $\pi/3$. Construct the dual basis.

4.3 Nickel atoms form a regular triangular array with an interatomic distance of 2.49 Å on the surface of a Nickel crystal. Particles with momentum $p = h/\lambda$ are incident on the crystal. Which conditions for coherent elastic scattering off the Nickel surface do we get for orthogonal incidence of the particle beam? Which conditions for coherent elastic scattering do we get for grazing incidence in the plane of the surface?

4.4 Suppose $V(\boldsymbol{x})$ is an analytic function of $\boldsymbol{x}$. Write down the $\boldsymbol{k}$-representation of the time-dependent and time-independent Schrödinger equations. Why is the $\boldsymbol{x}$-representation usually preferred for solving the Schrödinger equation?

4.5 Suppose that the Hamilton operator depends on a real parameter λ, $H = H(\lambda)$. This parameter dependence will influence the energy eigenvalues and eigenstates of the Hamiltonian,

$$H(\lambda)|\psi_n(\lambda)\rangle = E_n(\lambda)|\psi_n(\lambda)\rangle.$$

Use $\langle\psi_m(\lambda)|\psi_n(\lambda)\rangle = \delta_{mn}$ (this could also be a δ function normalization), to show that[3]

$$\delta_{mn}\frac{dE_n(\lambda)}{d\lambda} = \langle\psi_m(\lambda)|\frac{dH(\lambda)}{d\lambda}|\psi_n(\lambda)\rangle + (E_n - E_m)\,\langle\psi_m(\lambda)|\frac{d}{d\lambda}|\psi_n(\lambda)\rangle. \tag{4.36}$$

For $m = n$ discrete this is known as the Hellmann-Feynman theorem[4] [13]. The theorem is important for the calculation of forces in molecules.

[3] P. Güttinger, Diplomarbeit, ETH Zürich, Z. Phys. 73, 169 (1932). Exceptionally, there is *no* summation convention used in equation (4.36).

[4] R.P. Feynman, Phys. Rev. 56, 340 (1939).

4.6 We consider particles of mass m which are bound in a potential $V(\boldsymbol{x})$. The potential does not depend on m. How do the energy levels of the bound states change if we increase the mass of the particles?
The eigenstates for different energies will usually have different momentum uncertainties Δp. Do the energy levels with large or small Δp change more rapidly with mass?

4.7 Show that the free propagator (3.24,3.25) is the x representation of the one-dimensional free time evolution operator,

$$U(t) = \exp\left(-\mathrm{i}\frac{t-\mathrm{i}\epsilon}{2m\hbar}\mathrm{p}^2\right), \quad U(x-x',t) = \langle x|U(t)|x'\rangle.$$

Here a small negative imaginary part was added to the time variable to ensure convergence of a Gaussian integral.
Show also that the free time-evolution operator in three dimensions satisfies

$$\begin{aligned} U(\boldsymbol{x}-\boldsymbol{x}',t) &= \langle \boldsymbol{x}|\exp\left(-\mathrm{i}\frac{t-\mathrm{i}\epsilon}{2m\hbar}\mathbf{p}^2\right)|\boldsymbol{x}'\rangle \\ &= \sqrt{\frac{m}{2\pi\mathrm{i}\hbar(t-\mathrm{i}\epsilon)}}^{3} \exp\left(\mathrm{i}\frac{m}{2\hbar(t-\mathrm{i}\epsilon)}(\boldsymbol{x}-\boldsymbol{x}')^2\right). \end{aligned} \tag{4.37}$$

For later reference we also notice that this implies the formula

$$\begin{aligned} \exp\left(\mathrm{i}\hbar\frac{t-\mathrm{i}\epsilon}{2m}\frac{\partial^2}{\partial\boldsymbol{x}^2}\right)\delta(\boldsymbol{x}-\boldsymbol{x}') &= \sqrt{\frac{m}{2\pi\mathrm{i}\hbar(t-\mathrm{i}\epsilon)}}^{3} \\ &\quad\times \exp\left(\mathrm{i}\frac{m}{2\hbar(t-\mathrm{i}\epsilon)}(\boldsymbol{x}-\boldsymbol{x}')^2\right). \end{aligned} \tag{4.38}$$

4.8 Apply equation (4.32) in the case $V(\boldsymbol{x}) = 0$ to plane wave states. Show that in this case the left hand side does not vanish in the limit $E(\boldsymbol{k}) \to E(\boldsymbol{k}')$. Indeed, the equation remains correct in this case only *because* the left hand side does not vanish.

Chapter 5

Formal Developments

We have to go through a few more formalities before we can resume our discussion of quantum effects in physics. In particular, we need to address minimal uncertainties of observables in quantum mechanics, Fourier transformation from time to energy dependence, and transformation and solution properties of differential operators.

5.1 Uncertainty relations

The statistical interpretation of the wave function naturally implies uncertainty in an observable A_o if the wave function is not an eigenstate of the hermitian operator A that corresponds to A_o. Suppose that A has eigenvalues a_n,

$$A|\phi_n\rangle = a_n|\phi_n\rangle, \quad \langle\phi_m|\phi_n\rangle = \delta_{mn}.$$

Substitution of the expansion

$$|\psi\rangle = \sum_n |\phi_n\rangle\langle\phi_n|\psi\rangle$$

into the formula for the expectation value $\langle A\rangle = \langle\psi|A|\psi\rangle$ in the state $|\psi\rangle$ yields

$$\langle A\rangle = \sum_n a_n \left|\langle\phi_n|\psi\rangle\right|^2,$$

i.e. $\left|\langle\phi_n|\psi\rangle\right|^2$ is a probability that the value a_n for the observable A_o will be observed if the system is in the state $|\psi\rangle$.
If the distribution $\left|\langle\phi_n|\psi\rangle\right|^2$ is strongly concentrated around a particular index ℓ, then it is very likely that a measurement of A_o will find the value a_ℓ with very little uncertainty. However, if the probability distribution $\left|\langle\phi_n|\psi\rangle\right|^2$ covers a broad range of indices or has maxima e.g. for two separated indices, then there will be high uncertainty of the value of the observable A_o, and observation of A_o for many copies of the system in the state $|\psi\rangle$ will yield a large scatter of observed values.

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If A has a continuous spectrum of eigenvalues, e.g. if $A = \mathrm{x}$ is the operator for the location x of a particle in one dimension, then $|\langle x|\psi\rangle|^2\, dx$ is the probability to find the system with a value of x in the interval $[x, x + dx]$.
Heisenberg found in 1927 an intuitive estimate for the minimal product of uncertainties Δx and Δp in location and momentum of a particle[1]. His arguments were easily made rigorous and generalized to other pairs of observables using the statistical formalism of quantum mechanics.
Suppose that two observables A_o and B_o are represented by the two hermitian operators A and B. The expectation value of the observable A_o in a state $|\psi\rangle$ is

$$\langle A\rangle = \langle\psi|A|\psi\rangle,$$

and the uncertainty ΔA of the expectation value $\langle A\rangle$ is defined through

$$\Delta A^2 = \langle (A - \langle A\rangle)^2\rangle = \langle A^2\rangle - \langle A\rangle^2.$$

Minimal values of the uncertainty ΔA with which the observable A_o can be measured are directly related to the *commutator* of the operator A with other operators. The commutator of the two operators A and B is defined through

$$[A, B]|\psi\rangle \equiv AB|\psi\rangle - BA|\psi\rangle,$$

where $AB|\psi\rangle$ is the action of the operator B on the state $|\psi\rangle$ followed by the action of the operator A on the new state $|\psi'\rangle = B|\psi\rangle$.
The commutator of two hermitian operators yields a new hermitian operator C,

$$[A, B] = \mathrm{i}C,$$

and it is easy to show that the magnitude of the expectation value $\langle C\rangle$ yields a lower bound on the product of uncertainties $\Delta A \cdot \Delta B$,

$$\Delta A \Delta B \geq \frac{1}{2}|\langle C\rangle|. \tag{5.1}$$

For the proof of this relation, we use a real parameter ξ. The function

$$\begin{aligned} 0 \leq f(\xi) &= \langle (A - \langle A\rangle - \mathrm{i}\xi B + \mathrm{i}\xi\langle B\rangle)\,(A - \langle A\rangle + \mathrm{i}\xi B - \mathrm{i}\xi\langle B\rangle)\rangle \\ &= \Delta A^2 - \xi\langle C\rangle + \xi^2 \Delta B^2 \end{aligned} \tag{5.2}$$

has minimal value for

$$\xi = \frac{\langle C\rangle}{2\Delta B^2}$$

and substitution into (5.2) yields

$$0 \leq \Delta A^2 - \frac{\langle C\rangle^2}{4\Delta B^2}.$$

[1] W. Heisenberg, Z. Phys. 43, 172 (1927).

This implies the result (5.1).
For the inequality in equation (5.2) note that

$$\langle\psi|\,(A-\langle A\rangle-\mathrm{i}\xi B+\mathrm{i}\xi\langle B\rangle)\,(A-\langle A\rangle+\mathrm{i}\xi B-\mathrm{i}\xi\langle B\rangle)\,|\psi\rangle$$
$$=\left|(A-\langle A\rangle+\mathrm{i}\xi B-\mathrm{i}\xi\langle B\rangle)\,|\psi\rangle\right|^2.$$

Equation (5.1) implies for the operators x and p for location and momentum of a particle Heisenberg's uncertainty relation

$$\Delta x\Delta p\geq\frac{\hbar}{2}, \tag{5.3}$$

or in tensorial form for the three-dimensional operators $\mathbf{x}$ and $\mathbf{p}$

$$\Delta\boldsymbol{x}\otimes\Delta\boldsymbol{p}\geq\frac{\hbar}{2}\underline{1}$$

If the state $|\psi\rangle$ should satisfy the uncertainty relation for $\Delta A\cdot\Delta B$ with the equality sign (minimal product of uncertainties), then we must have

$$\begin{aligned}0&=\langle\psi|\left[(A-\langle A\rangle)^2-\frac{\langle C\rangle^2}{4\Delta B^4}\,(B-\langle B\rangle)^2\right]|\psi\rangle\\&=\langle\psi|\left[A-\langle A\rangle-\mathrm{i}\langle C\rangle\frac{B-\langle B\rangle}{2\Delta B^2}\right]\left[A-\langle A\rangle+\mathrm{i}\langle C\rangle\frac{B-\langle B\rangle}{2\Delta B^2}\right]|\psi\rangle\\&=\left|\left[A-\langle A\rangle+\mathrm{i}\langle C\rangle\frac{B-\langle B\rangle}{2\Delta B^2}\right]|\psi\rangle\right|^2,\end{aligned}$$

where in the second equation the commutator $[A,B]=\mathrm{i}C$ has been used. This is equivalent to

$$\left[A-\langle A\rangle+\mathrm{i}\langle C\rangle\frac{B-\langle B\rangle}{2\Delta B^2}\right]|\psi\rangle=0.$$

In particular we have minimal $\Delta p\Delta x$ if and only if

$$\left[p-p_0-\mathrm{i}\hbar\frac{x-x_0}{2\Delta x^2}\right]|\psi\rangle=0. \tag{5.4}$$

This implies in the x-representation

$$\left[\frac{d}{dx}-\mathrm{i}\frac{p_0}{\hbar}+\frac{x-x_0}{2\Delta x^2}\right]\langle x|\psi\rangle=0$$

and yields up to an arbitrary constant phase factor the Gaussian wave packet (3.31)

$$\langle x|\psi\rangle=\frac{1}{(2\pi\Delta x^2)^{1/4}}\exp\left(-\frac{(x-x_0)^2}{4\Delta x^2}+\mathrm{i}\frac{p_0x}{\hbar}-\mathrm{i}\frac{p_0x_0}{2\hbar}\right). \tag{5.5}$$

Equation (5.4) is in p-representation

$$\left[2\Delta x^2(p-p_0)+\mathrm{i}\hbar x_0+\hbar^2\frac{d}{dp}\right]\langle p|\psi\rangle=0,$$

and this yields (again up to an arbitrary constant phase factor)

$$\langle p|\psi\rangle=\left(\frac{2\Delta x^2}{\pi\hbar^2}\right)^{\frac{1}{4}}\exp\left(-\frac{\Delta x^2}{\hbar^2}(p-p_0)^2-\mathrm{i}\frac{px_0}{\hbar}+\mathrm{i}\frac{p_0x_0}{2\hbar}\right),\tag{5.6}$$

which explicitly confirms

$$\Delta p=\frac{\hbar}{2\Delta x}$$

and corresponds to the wave packet (3.32).
For comparison of the solutions, we note that

$$\begin{aligned}\langle p|\psi\rangle&=\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}dx\,\exp\left(-\mathrm{i}\frac{px}{\hbar}\right)\langle x|\psi\rangle\\&=\frac{1}{\sqrt{2\pi\hbar}}\frac{1}{(2\pi\Delta x^2)^{1/4}}\\&\quad\times\int_{-\infty}^{\infty}dx\,\exp\left[-\frac{1}{4\Delta x^2}\left(x-x_0+\mathrm{i}\frac{2\Delta x^2}{\hbar}(p-p_0)\right)^2\right]\\&\quad\times\exp\left(-\frac{\Delta x^2}{\hbar^2}(p-p_0)^2-\mathrm{i}\frac{(p-p_0)x_0}{\hbar}\right)\\&=\left(\frac{2\Delta x^2}{\pi\hbar^2}\right)^{\frac{1}{4}}\exp\left(-\frac{\Delta x^2}{\hbar^2}(p-p_0)^2-\mathrm{i}\frac{px_0}{\hbar}+\mathrm{i}\frac{p_0x_0}{2\hbar}\right).\end{aligned}$$

The phase factor $\exp(-\mathrm{i}p_0x_0/2\hbar)$ was included in in (5.5) to ensure that (5.5) and (5.6) are also related through direct Fourier transform. Otherwise there would have been a mismatch in a phase $\propto p_0x_0/2\hbar$.
We have seen in equation (3.35) that the width Δx^2 will remain minimal only for a certain moment in time if a Gaussian packet follows a free evolution $\mathrm{i}d|\psi(t)\rangle/dt\propto p^2|\psi(t)\rangle$, while the uncertainty Δp^2 in momentum remains constant. Therefore a freely evolving Gaussian packet will satisfy the minimal condition $\Delta x\Delta p=\hbar/2$ only for a moment in time.
A Gaussian wave packet following an evolution $\mathrm{i}d|\psi(t)\rangle/dt\propto x^2|\psi(t)\rangle$ would have constant Δx^2, but Δp^2 would have the minimal possible value $\hbar/(2\Delta x)$ only for a moment in time. Such a hypothetical quantum system would correspond to an oscillator without kinetic energy, and it could move uniformly along the p axis.
In Chapter 6 we will find that a harmonic oscillator evolution for Gaussian wave packets, $\mathrm{i}d|\psi(t)\rangle/dt=(\alpha p^2+\beta x^2)|\psi(t)\rangle$, yields constant widths both in x and in p direction, and the minimal uncertainty condition $\Delta x\Delta p=\hbar/2$ will be satisfied at all times.

There is also an uncertainty relation between energy and time, which is not as strict as the relations (5.1, 5.3), and cannot be proven by the same rigorous mathematical methods. The relation involves the minimal time window Δt which is required to observe a system with energy uncertainty ΔE. Smaller energy uncertainty requires a longer observation window, or a longer time to form the system,

$$\Delta t \Delta E \gtrsim \mathcal{O}(\hbar). \tag{5.7}$$

This order of magnitude estimate is often written as

$$\Delta t \Delta E \gtrsim \frac{\hbar}{2},$$

for symmetry with the Heisenberg uncertainty relation (5.3), but it should not be mistaken to indicate a strict lower bound as in equation (5.3).
Equation (5.7) cannot be derived in the same way as equation (5.3) because time is not an observable, but a parameter in quantum mechanics. Therefore there is no related expectation value, nor is there any corresponding definition of Δt as the variance of an expectation value.
There exist a few simple heuristic derivations to motivate equation (5.7) from equation (5.3), but we will find the best justifications for (5.7) in the equations of time-dependent perturbation theory in Chapter 13.

5.2 Energy representation and energy-time Fourier transformation

Fourier transformation from $\boldsymbol{x}$-dependent wave functions $\psi(\boldsymbol{x}, t)$ to $(\boldsymbol{k} = \boldsymbol{p}/\hbar)$-dependent wave functions $\psi(\boldsymbol{k}, t)$ is defined within the framework of classical analysis as long as we are only dealing with square integrable functions, which is the case for bound states. However, even for Fourier transformation between the $\boldsymbol{x}$ and $\boldsymbol{p}$ representations of wave functions we had to go beyond classical analysis and invoke the δ function to deal e.g. with plane wave states.
Fourier transformation of wave functions between energy and time is also important in quantum mechanics, but it is clear that we always have to define it in terms of distributions when it comes to the energy representation, because wave functions $\psi(\boldsymbol{x}, t)$ are never square integrable (nor e.g. absolutely integrable) with respect to time. Therefore the standard classical criteria for existence of Fourier transforms from t to $\omega = E/\hbar$ in the sense of classical analysis will never apply for a quantum system. In spite of this verdict, we will see that time-energy Fourier transformation automatically appears in quantum mechanics if we combine completeness of energy eigenstates with the time evolution implied by the Schrödinger equation.
Recall that the eigenstates of a stationary Hamiltonian,

$$H|\psi_\alpha\rangle = E_\alpha|\psi_\alpha\rangle$$

form a complete basis,

$$\sum\!\!\!\!\!\!\int d\alpha\, |\psi_\alpha\rangle\langle\psi_\alpha| = 1, \tag{5.8}$$

see Section 2.2 and Appendix C. The notation $\sum\!\!\!\!\!\!\int d\alpha$ stands for summation over discrete quantum numbers and integration over continuous quantum numbers, see e.g. (3.20), which we can write in bra-ket notation in the form

$$|\kappa\rangle\langle\kappa| + \int_0^\infty dk\, (|k,-\rangle\langle k,-| + |k,+\rangle\langle k,+|) = 1.$$

Another example is the completeness of the states (3.10) in a cubic quantum wire,

$$\sum_{n_1=1}^\infty \sum_{n_2=1}^\infty \int_{-\infty}^\infty dk\, |n_1, n_2, k\rangle\langle n_1, n_2, k| = 1.$$

On the other hand, for every time-dependent state which evolves with the Hamiltonian H, the Schrödinger equation

$$\mathrm{i}\hbar \frac{d}{dt}|\psi(t)\rangle = H|\psi(t)\rangle$$

implies

$$|\psi(t)\rangle = \exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right)|\psi(0)\rangle. \tag{5.9}$$

Substitution of the decomposition $|\psi(0)\rangle = \sum\!\!\!\!\!\!\int d\alpha |\psi_\alpha\rangle\langle\psi_\alpha|\psi(0)\rangle$ into (5.9) yields

$$|\psi(t)\rangle = \sum\!\!\!\!\!\!\int d\alpha\, |\psi_\alpha\rangle\langle\psi_\alpha|\psi(0)\rangle \exp\left(-\frac{\mathrm{i}}{\hbar}E_\alpha t\right).$$

We can interprete this as an energy-time Fourier transformation

$$|\psi(t)\rangle = \frac{1}{2\pi\hbar}\int dE\, |\psi(E)\rangle \exp\left(-\frac{\mathrm{i}}{\hbar}Et\right) \tag{5.10}$$

with inversion

$$|\psi(E)\rangle = \int dt\, |\psi(t)\rangle \exp\left(\frac{\mathrm{i}}{\hbar}Et\right) \tag{5.11}$$

if we define

$$\begin{aligned} |\psi(E)\rangle &= 2\pi\hbar \sum\!\!\!\!\!\!\int d\alpha\, |\psi_\alpha\rangle\langle\psi_\alpha|\psi(0)\rangle\delta(E - E_\alpha) \\ &= 2\pi\hbar\delta(E - H)|\psi(t=0)\rangle. \end{aligned} \tag{5.12}$$

Although the Fourier transformation from $|\psi(t)\rangle$ to an energy-dependent state does not exist in the sense of classical Fourier theory, it exists as a sum of δ functions over the energy spectrum of the Hamiltonian.
The energy expectation value in the state $|\psi(t)\rangle$ is

$$\langle E\rangle = \langle\psi(t)|H|\psi(t)\rangle = \sum\!\!\!\!\!\!\int d\alpha\, E_\alpha\, |\langle\psi_\alpha|\psi(0)\rangle|^2 .$$

The corresponding energy uncertainty ΔE follows from

$$\Delta E^2 = \sum\!\!\!\!\!\!\int d\alpha\, E_\alpha^2\, |\langle\psi_\alpha|\psi(0)\rangle|^2 - \left(\sum\!\!\!\!\!\!\int d\alpha\, E_\alpha\, |\langle\psi_\alpha|\psi(0)\rangle|^2\right)^2 .$$

5.3 Dimensions of states

A simple, but useful concept for checking consistency in quantum mechanical calculations is the concept of length dimension of a state. To introduce this concept, note that the completeness relation for the eigenstates of the one-dimensional attractive δ potential

$$|\kappa\rangle\langle\kappa| + \int_0^\infty dk\, (|k,-\rangle\langle k,-| + |k,+\rangle\langle k,+|) = 1$$

implies that the discrete bound state $|\kappa\rangle$ is dimensionless, while the continuous unbound states $|k,\pm\rangle$ have the dimension of length$^{1/2}$.
Similarly, the completeness relations for continuous one-dimensional x or free momentum eigenstates

$$\int dx\, |x\rangle\langle x| = 1, \quad \int dk\, |k\rangle\langle k| = 1 \tag{5.13}$$

imply that $|x\rangle$ has the dimension of length$^{-1/2}$ and $|k\rangle$ has the dimension of length$^{1/2}$. The wave functions $\langle x|\kappa\rangle$ and $\langle k|\kappa\rangle$ therefore have dimension of length$^{-1/2}$ or dimension of length$^{1/2}$, respectively, while the representations or wave functions $\langle x|k\rangle$ or $\langle x|k,\pm\rangle$ are dimensionless. The momentum representations of the unbound states of the attractive δ potential,

$$\langle k'|k,\pm\rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx\, \exp(-\mathrm{i}k'x)\psi_{k,\pm}(x)$$

have length dimension 1, e.g.

$$\langle k'|k,-\rangle = \frac{1}{\mathrm{i}\sqrt{2}} \left[\delta(k-k') - \delta(k+k')\right].$$

In three dimensions, the states $|n_1,n_2,n_3\rangle$ in a cubic quantum dot are dimensionless while the states $|n_1,n_2,k\rangle$ (3.10) in a cubic quantum wire have the dimension of length$^{1/2}$ in agreement with their completeness relation

$$\sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\int_{-\infty}^{\infty} dk\, |n_1,n_2,k\rangle\langle n_1,n_2,k| = 1.$$

The continuous state $|\boldsymbol{x}\rangle$ apparently has dimension of length$^{-3/2}$ and $|\boldsymbol{k}\rangle$ has the dimension of length$^{3/2}$. The representation $\langle\boldsymbol{x}|\boldsymbol{k}\rangle$ of a plane wave state is therefore dimensionless, while the representation $\langle\boldsymbol{x}|n_1, n_2, n_3\rangle$ of a quantum dot state has the dimension length$^{-3/2}$.
A state $|\psi\rangle$ in d spatial dimensions is usually specified in terms of $N \geq d$ quantum numbers. If c_k of these quantum numbers are continuous wave-number like quantum numbers and c_x quantum numbers are continuous position like quantum numbers, the length dimension of the state is length$^{(c_k - c_x)/2}$. The representation (= transformation matrix element = wave function) $\langle\psi|\psi'\rangle$ has length dimension length$^{(c_k + c'_k - c_x - c'_x)/2}$. This is as trivial as calculating with units, and as useful for checking consistency of results.

5.4 Gradients and Laplace operators in general coordinate systems

The transformation properties of the gradient $\boldsymbol{\nabla}$ and Laplace operator $\Delta = \boldsymbol{\nabla}^2$ under coordinate transformations are basic aspects of mathematics that we have to discuss due to the importance of those operators in quantum mechanics. We use three dimensions for the discussions in this section, but the methods apply in any number of dimensions.
Suppose we wish to use coordinates ξ^α, $1 \leq \alpha \leq 3$, instead of Cartesian coordinates x^i. The coordinate maps

$$\xi^\alpha \to x^i(\boldsymbol{\xi}), \quad x^i \to \xi^\alpha(\boldsymbol{x}) \tag{5.14}$$

define Jacobi matrices

$$\partial_\alpha x^i(\boldsymbol{\xi}) \equiv \frac{\partial x^i(\boldsymbol{\xi})}{\partial \xi^\alpha} \tag{5.15}$$

and $\partial_i \xi^\alpha(\boldsymbol{x})$. The Jacobi matrix (5.15) in particular allows us to calculate tangent vectors to the new x^i coordinate lines. We can easily figure this out by observing that the map (5.14) can be written as (recall summation convention)

$$\xi^\alpha \to \boldsymbol{r}(\boldsymbol{\xi}) = x^i(\boldsymbol{\xi})\boldsymbol{e}_i,$$

where the vectors $\boldsymbol{e}_i$ are the Cartesian basis vectors along the x^i coordinate lines. Infinitesimal coordinate shifts generate a vector

$$d\boldsymbol{r} = dx^i \boldsymbol{e}_i = d\xi^\alpha \partial_\alpha x^i \boldsymbol{e}_i = \boldsymbol{a}_\alpha d\xi^\alpha,$$

and this tells us that the vector

$$\boldsymbol{a}_\alpha(\boldsymbol{\xi}) = \partial_\alpha \boldsymbol{r}(\boldsymbol{\xi}) = \partial_\alpha x^i(\boldsymbol{\xi})\boldsymbol{e}_i. \tag{5.16}$$

is a tangent vector along the ξ^α coordinate line in the point $\boldsymbol{r}(\boldsymbol{\xi})$.

The products of these tangent vectors define the components of the metric in the new coordinate system,

$$g_{\alpha\beta}(\boldsymbol{\xi}) = \boldsymbol{a}_\alpha(\boldsymbol{\xi}) \cdot \boldsymbol{a}_\beta(\boldsymbol{\xi}),$$

because the length squared of the shift vector $d\boldsymbol{r}$ is

$$ds^2 = d\boldsymbol{r}^2 = \boldsymbol{a}_\alpha \cdot \boldsymbol{a}_\beta d\xi^\alpha d\xi^\beta = g_{\alpha\beta} d\xi^\alpha d\xi^\beta.$$

The inverse metric $g^{\alpha\beta}$ yields the dual basis vectors according to equations (4.8,4.9),

$$\boldsymbol{a}^\alpha(\boldsymbol{\xi}) = g^{\alpha\beta}(\boldsymbol{\xi}) \boldsymbol{a}_\beta(\boldsymbol{\xi}),$$

and the Jacobian matrix $\partial_i \xi^\alpha(\boldsymbol{x})$ connects the dual basis vectors,

$$\boldsymbol{a}^\alpha = \boldsymbol{e}^i \partial_i \xi^\alpha. \tag{5.17}$$

Simple consequences of $\boldsymbol{a}_\alpha(\boldsymbol{\xi}) = \partial_\alpha \boldsymbol{r}(\boldsymbol{\xi})$ and $\boldsymbol{a}^\alpha(\boldsymbol{\xi}) \cdot \boldsymbol{a}_\beta(\boldsymbol{\xi}) = \delta^\alpha{}_\beta$ are

$$\partial_\alpha \boldsymbol{a}_\beta = \partial_\beta \boldsymbol{a}_\alpha$$

and

$$\boldsymbol{a}^\alpha \cdot \partial_\gamma \boldsymbol{a}_\beta = -\boldsymbol{a}_\beta \cdot \partial_\gamma \boldsymbol{a}^\alpha.$$

The $\boldsymbol{\nabla}$ operator is defined as

$$\boldsymbol{\nabla} = \boldsymbol{e}^i \frac{\partial}{\partial x^i} = \boldsymbol{e}^i \frac{\partial \xi^\alpha}{\partial x^i} \frac{\partial}{\partial \xi^\alpha} = \boldsymbol{a}^\alpha \frac{\partial}{\partial \xi^\alpha}. \tag{5.18}$$

Note that once we accept the Cartesian equation $\boldsymbol{\nabla} = \boldsymbol{e}^i \partial_i$ with the recognition that the Cartesian vectors $\boldsymbol{e}^i = \boldsymbol{e}_i$ appearing in the $\boldsymbol{\nabla}$ operator are actually the dual basis vectors, the representation $\boldsymbol{\nabla} = \boldsymbol{a}^\alpha \partial_\alpha$ in the new coordinate system is a direct consequence of the chain rule of differentiation. Furthermore, we can write equation (5.17) also in the form

$$\boldsymbol{a}^\alpha = \boldsymbol{\nabla} \xi^\alpha \tag{5.19}$$

and the inverse metric is

$$g^{\alpha\beta} = (\boldsymbol{\nabla} \xi^\alpha) \cdot (\boldsymbol{\nabla} \xi^\beta). \tag{5.20}$$

These equations are particularly convenient if the new coordinates are given in terms of the Cartesian coordinates x^i, $\xi^\alpha = \xi^\alpha(\boldsymbol{x})$.
The new dual basis vectors $\boldsymbol{a}^\alpha = \boldsymbol{a}^\alpha(\boldsymbol{\xi})$ generically depend on the coordinates $\boldsymbol{\xi}$, because the new coordinates will often be curvilinear. We have to take this into account when calculating the Laplace operator in the new coordinate system,

$$\Delta = \boldsymbol{\nabla}^2 = \boldsymbol{a}^\alpha(\boldsymbol{\xi}) \partial_\alpha \circ \boldsymbol{a}^\beta(\boldsymbol{\xi}) \partial_\beta = g^{\alpha\beta}(\boldsymbol{\xi}) \partial_\alpha \partial_\beta + \boldsymbol{a}^\alpha(\boldsymbol{\xi}) \cdot (\partial_\alpha \boldsymbol{a}^\beta(\boldsymbol{\xi})) \partial_\beta. \tag{5.21}$$

We can also write this as

$$\Delta = g^{\alpha\beta}(\boldsymbol{\xi})\left(\partial_\alpha\partial_\beta + \boldsymbol{a}_\beta(\boldsymbol{\xi})\cdot\partial_\alpha\boldsymbol{a}^\gamma(\boldsymbol{\xi})\partial_\gamma\right) = g^{\alpha\beta}(\boldsymbol{\xi})\left(\partial_\alpha\partial_\beta - \Gamma^\gamma{}_{\beta\alpha}(\boldsymbol{\xi})\partial_\gamma\right),$$

where the coefficients

$$\Gamma^\gamma{}_{\beta\alpha}(\boldsymbol{\xi}) = -\boldsymbol{a}_\beta(\boldsymbol{\xi})\cdot\partial_\alpha\boldsymbol{a}^\gamma(\boldsymbol{\xi}) = \boldsymbol{a}^\gamma(\boldsymbol{\xi})\cdot\partial_\alpha\boldsymbol{a}_\beta(\boldsymbol{\xi}) \tag{5.22}$$

are known as *Christoffel symbols*.
We can use equation (5.21) e.g. to calculate the Laplace operator in spherical coordinates. It is convenient to use the common column vector notation for components with respect to the Cartesian $\boldsymbol{e}_i = \boldsymbol{e}^i$ in the actual calculaton. The transformation

$$\boldsymbol{r} = \begin{pmatrix} x^1 \\ x^2 \\ x^3 \end{pmatrix} = \begin{pmatrix} r\sin\vartheta\,\cos\varphi \\ r\sin\vartheta\,\sin\varphi \\ r\cos\vartheta \end{pmatrix}$$

yields tangent vectors

$$\boldsymbol{a}_r = \partial_r\boldsymbol{r} = \begin{pmatrix} \sin\vartheta\,\cos\varphi \\ \sin\vartheta\,\sin\varphi \\ \cos\vartheta \end{pmatrix}, \quad \boldsymbol{a}_\vartheta = \partial_\vartheta\boldsymbol{r} = \begin{pmatrix} r\cos\vartheta\,\cos\varphi \\ r\cos\vartheta\,\sin\varphi \\ -r\sin\vartheta \end{pmatrix},$$

and

$$\boldsymbol{a}_\varphi = \partial_\varphi\boldsymbol{r} = \begin{pmatrix} -r\sin\vartheta\,\sin\varphi \\ r\sin\vartheta\,\cos\varphi \\ 0 \end{pmatrix}.$$

The metric and the inverse metric in spherical coordinates are

$$\underline{g} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & r^2 & 0 \\ 0 & 0 & r^2\sin^2\vartheta \end{pmatrix}, \quad \underline{g}^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & r^{-2} & 0 \\ 0 & 0 & r^{-2}\sin^{-2}\vartheta \end{pmatrix},$$

and the dual vectors are

$$\boldsymbol{a}^r = \begin{pmatrix} \sin\vartheta\,\cos\varphi \\ \sin\vartheta\,\sin\varphi \\ \cos\vartheta \end{pmatrix}, \quad \boldsymbol{a}^\vartheta = \frac{1}{r}\begin{pmatrix} \cos\vartheta\,\cos\varphi \\ \cos\vartheta\,\sin\varphi \\ -\sin\vartheta \end{pmatrix},$$

$$\boldsymbol{a}^\varphi = \frac{1}{r\sin\vartheta}\begin{pmatrix} -\sin\varphi \\ \cos\varphi \\ 0 \end{pmatrix}.$$

The non-vanishing products

$$\boldsymbol{a}^\vartheta\cdot\partial_\vartheta\boldsymbol{a}^r = \boldsymbol{a}^\varphi\cdot\partial_\varphi\boldsymbol{a}^r = \frac{1}{r}, \quad \boldsymbol{a}^\varphi\cdot\partial_\varphi\boldsymbol{a}^\vartheta = \frac{\cot\vartheta}{r^2}$$

yield

$$\Delta = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \vartheta^2} + \frac{\cot\vartheta}{r^2}\frac{\partial}{\partial \vartheta} + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial \varphi^2}. \tag{5.23}$$

Later we will also use the normalized spherical tangent vectors

$$\boldsymbol{e}_r \equiv \boldsymbol{a}_r, \quad \boldsymbol{e}_\vartheta = \frac{1}{r}\boldsymbol{a}_\vartheta, \quad \boldsymbol{e}_\varphi = \frac{1}{r\sin\vartheta}\boldsymbol{a}_\varphi.$$

Another useful representation of the Laplace operator which follows from equation (5.21) is

$$\Delta = \frac{1}{\sqrt{g}}\partial_\alpha\big(\sqrt{g}g^{\alpha\beta}\partial_\beta\big), \tag{5.24}$$

where $g(\boldsymbol{\xi})$ is the determinant of the metric tensor $g_{\alpha\beta}(\boldsymbol{\xi})$. To demonstrate equivalence of (5.24) with (5.21) one has to use the properties

$$\partial_\alpha g = g g^{\beta\gamma}\partial_\alpha g_{\beta\gamma} = -g g_{\beta\gamma}\partial_\alpha g^{\beta\gamma}$$

and

$$g_{\beta\gamma}\partial_\alpha g^{\beta\gamma} = 2\boldsymbol{a}_\gamma\cdot\partial_\alpha\boldsymbol{a}^\gamma = -2\boldsymbol{a}^\gamma\cdot\partial_\alpha\boldsymbol{a}_\gamma = -2\boldsymbol{a}^\gamma\cdot\partial_\gamma\boldsymbol{a}_\alpha = 2\boldsymbol{a}_\alpha\cdot\partial_\gamma\boldsymbol{a}^\gamma.$$

It is also useful to point out that $\sqrt{g}(\boldsymbol{\xi})$ is the volume measure in the new coordinates ξ^α,

$$d^3\boldsymbol{x} = dx^1dx^2dx^3 = d\xi^1d\xi^2d\xi^3\sqrt{g}(\boldsymbol{\xi}). \tag{5.25}$$

This follows from the fact that the matrix relation

$$g_{\alpha\beta}(\boldsymbol{\xi}) = \partial_\alpha\boldsymbol{r}(\boldsymbol{\xi})\cdot\partial_\beta\boldsymbol{r}(\boldsymbol{\xi}) = \partial_\alpha x^i(\boldsymbol{\xi})\cdot\partial_\beta x^j(\boldsymbol{\xi})\delta_{ij}$$

implies that the determinant $g = \det(g_{\alpha\beta})$ is the square of the Jacobian determinant,

$$g(\boldsymbol{\xi}) = \big(\det(\partial_\alpha x^i(\boldsymbol{\xi}))\big)^2, \tag{5.26}$$

and the familiar form for transformation of volume measures,

$$dx^1dx^2dx^3 = d\xi^1d\xi^2d\xi^3\,\big|\det(\partial_\alpha x^i(\boldsymbol{\xi}))\big|, \tag{5.27}$$

then yields (5.25).

5.5 Separation of differential equations

Separation of variables, where applicable, is a very powerful and useful tool for solution of partial differential equations. The purpose of this section is to point out that separation of variables for separable hermitian operators is not just a matter of convenient choice, but a must for the determination of eigenfunctions of these operators. Eigenstates of separable hermitian differential operators will automatically factorize into eigenstates of the corresponding lower-dimensional operators.

We assume a three-dimensional space with coordinates ξ^i, $1 \leq i \leq 3$, but the reader will again recognize that the arguments presented in this section do not depend on the number of dimensions.

In quantum mechanics we often encounter Hamiltonians with the following property: If we choose a suitable set of coordinates $\boldsymbol{\xi}$, then the time-independent Schrödinger equation

$$E|\psi(E)\rangle = H|\psi(E)\rangle$$

will separate in the form

$$E\langle\boldsymbol{\xi}|\psi(E)\rangle = \sum_i \langle\boldsymbol{\xi}|H_i|\psi(E)\rangle = \sum_i \mathcal{D}_i\langle\boldsymbol{\xi}|\psi(E)\rangle, \tag{5.28}$$

where each of the hermitian differential operators $\mathcal{D}_i$ has the property to contain only the coordinate ξ_i and the corresponding derivative $\partial/\partial\xi^i$. However, the results on completeness of eigenstates of one-dimensional hermitian operators from Appendix C imply that each of the operators has its own complete set of eigenfunctions,

$$\mathcal{D}_i\langle\xi_i|\psi_i(E_i)\rangle = E_i\langle\xi_i|\psi_i(E_i)\rangle, \tag{5.29}$$

where the different eigenfunctions $\langle\xi_i|\psi_i(E_i)\rangle$ are labeled by the eigenvalues E_i.

This can give us the idea to decompose the function $\langle\boldsymbol{\xi}|\psi(E)\rangle$ with respect to the eigenfunctions $\langle\xi_1|\psi_1(E_1)\rangle$,

$$\langle\boldsymbol{\xi}|\psi(E)\rangle = \sum\!\!\!\!\!\!\int dE_1\, \langle\xi_1|\psi_1(E_1)\rangle\langle E_1, \xi_2, \xi_3|\psi(E)\rangle,$$

$$\langle E_1, \xi_2, \xi_3|\psi(E)\rangle = \int d\xi_1\, \langle\psi_1(E_1)|\xi_1\rangle\langle\xi_1, \xi_2, \xi_3|\psi(E)\rangle.$$

We can then repeat the decomposition with respect to the eigenfunctions of $\mathcal{D}_2$ and $\mathcal{D}_3$. This leads finally to the decomposition

$$\begin{aligned}\langle\boldsymbol{\xi}|\psi(E)\rangle = {} & \sum\!\!\!\!\!\!\int dE_1 \sum\!\!\!\!\!\!\int dE_2 \sum\!\!\!\!\!\!\int dE_3\, \langle\xi_1|\psi_1(E_1)\rangle\langle\xi_2|\psi_2(E_2)\rangle\langle\xi_3|\psi_3(E_3)\rangle \\ & \times \langle E_1, E_2, E_3|\psi(E)\rangle,\end{aligned} \tag{5.30}$$

$$\langle E_1, E_2, E_3|\psi(E)\rangle = \int d\xi_1 \int d\xi_2 \int d\xi_3 \, \langle \psi_1(E_1)|\xi_1\rangle\langle\psi_2(E_2)|\xi_2\rangle \times \langle\psi_3(E_3)|\xi_3\rangle\langle\xi_1,\xi_2,\xi_3|\psi(E)\rangle.$$

Substitution of the decomposition (5.30) into the Schrödinger equation (5.28) yields

$$\begin{aligned} & E \iiint dE_1 \iiint dE_2 \iiint dE_3 \, \langle\xi_1|\psi_1(E_1)\rangle\langle\xi_2|\psi_2(E_2)\rangle\langle\xi_3|\psi_3(E_3)\rangle \\ & \times\langle E_1, E_2, E_3|\psi(E)\rangle \\ & = \iiint dE_1 \iiint dE_2 \iiint dE_3 \, (E_1+E_2+E_3) \, \langle\xi_1|\psi_1(E_1)\rangle\langle\xi_2|\psi_2(E_2)\rangle\langle\xi_3|\psi_3(E_3)\rangle \\ & \times\langle E_1, E_2, E_3|\psi(E)\rangle. \end{aligned} \tag{5.31}$$

The orthogonality properties of different eigenfunctions,

$$\int d\xi_i \, \langle\psi_i(E_i)|\xi_i\rangle\langle\xi_i|\psi_i(E_i')\rangle\Big|_{E_i\neq E_i'} = 0$$

then imply that for all combinations of eigenvalues E and E_i the condition

$$\begin{aligned} & (E_1 + E_2 + E_3 - E) \, \langle\xi_1|\psi_1(E_1)\rangle\langle\xi_2|\psi_2(E_2)\rangle\langle\xi_3|\psi_3(E_3)\rangle \\ & \times\langle E_1, E_2, E_3|\psi(E)\rangle = 0 \end{aligned}$$

must be satisfied, i.e. the eigenvalue E in equation (5.31) must equal one particular sum of eigenvalues,

$$E = E_1 + E_2 + E_3, \tag{5.32}$$

and the related eigenfunction is

$$\langle\boldsymbol{\xi}|\psi(E)\rangle = \langle\xi_1|\psi_1(E_1)\rangle\langle\xi_2|\psi_2(E_2)\rangle\langle\xi_3|\psi_3(E_3)\rangle. \tag{5.33}$$

These observations tell us that we can and indeed should use a separation ansatz for Hamiltonians of the form (5.28).
The previous argument works for Hamiltonian operators which split into a sum of one-dimensional operators in suitable coordinates. However, the arguments are easily generalized to the more general case

$$\begin{aligned} E\langle\boldsymbol{\xi}|\psi(E)\rangle = {} & f(\xi_3)g(\xi_2)\mathcal{D}_1\langle\boldsymbol{\xi}|\psi(E)\rangle + f(\xi_3)\mathcal{D}_2\langle\boldsymbol{\xi}|\psi(E)\rangle \\ & +\mathcal{D}_3\langle\boldsymbol{\xi}|\psi(E)\rangle. \end{aligned} \tag{5.34}$$

Since $\mathcal{D}_1$ commutes with the Hamiltonian operator on the right hand side, the space of eigenfunctions $\langle\boldsymbol{\xi}|\psi(E)\rangle$ with fixed eigenvalue E must be generated by a set of eigenstates of the hermitian differential operator $\mathcal{D}_1$ with eigenvalues $\tilde{E}_1$,

$$\langle\boldsymbol{\xi}|\psi(E)\rangle = \iint d\tilde{E}_1 \, \langle\xi_1|\psi_1(\tilde{E}_1)\rangle\langle\tilde{E}_1,\xi_2,\xi_3|\psi(E)\rangle.$$

Non-degeneracy of the one-dimensional eigenvalues $\tilde{E}_1$ and linear independence of the corresponding eigenstates then implies

$$E\langle\tilde{E}_1,\xi_2,\xi_3|\psi(E)\rangle = f(\xi_3)\left[g(\xi_2)\tilde{E}_1+\mathcal{D}_2\right]\langle\tilde{E}_1,\xi_2,\xi_3|\psi(E)\rangle + \mathcal{D}_3\langle\tilde{E}_1,\xi_2,\xi_3|\psi(E)\rangle.$$

Now the Hamiltonian on the right hand side commutes with the parameter-dependent hermitian one-dimensional operator

$$\mathcal{D}_2' = \mathcal{D}_2 + g(\xi_2)\tilde{E}_1,$$

which has parameter-dependent eigenvalues $\tilde{E}_2(\tilde{E}_1)$. The further decomposition

$$\langle\boldsymbol{\xi}|\psi(E)\rangle = \sum\!\!\!\!\!\!\int d\tilde{E}_1 \sum\!\!\!\!\!\!\int d\tilde{E}_2(\tilde{E}_1)\,\langle\xi_1|\psi_1(\tilde{E}_1)\rangle\langle\xi_2|\psi_2'(\tilde{E}_2(\tilde{E}_1))\rangle \times\langle\tilde{E}_1,\tilde{E}_2(\tilde{E}_1),\xi_3|\psi(E)\rangle$$

then yields the one-dimensional hermitian problem

$$E\langle\tilde{E}_1,\tilde{E}_2(\tilde{E}_1),\xi_3|\psi(E)\rangle = f(\xi_3)\tilde{E}_2(\tilde{E}_1)\langle\tilde{E}_1,\tilde{E}_2(\tilde{E}_1),\xi_3|\psi(E)\rangle + \mathcal{D}_3\langle\tilde{E}_1,\tilde{E}_2(\tilde{E}_1),\xi_3|\psi(E)\rangle,$$

which finally yields eigenvalues $E_n(\tilde{E}_1,\tilde{E}_2)$ and the solution

$$\langle\boldsymbol{\xi}|\psi(E_n(\tilde{E}_1,\tilde{E}_2))\rangle = \langle\xi_1|\psi_1(\tilde{E}_1)\rangle\langle\xi_2|\psi_2'(\tilde{E}_2(\tilde{E}_1))\rangle \times\langle\tilde{E}_1,\tilde{E}_2(\tilde{E}_1),\xi_3|\psi(E_n(\tilde{E}_1,\tilde{E}_2))\rangle. \tag{5.35}$$

5.6 Problems

5.1 We consider a particle of mass m in a one-dimensional infinite square well, i.e. the energy eigenstates $|n\rangle$ are labelled by natural numbers n. How large are the energy expectation value and energy uncertainty in the state

$$|\psi\rangle = \sqrt{e-1}\sum_{n=1}^{\infty}\exp(-n/2)|n\rangle?$$

5.2 Calculate the Laplace operator in spherical coordinates from equation (5.24).

5.3 Calculate the tangent vectors, the $\boldsymbol{\nabla}$ operator and the Laplace operator in parabolic coordinates

$$x = 2\sqrt{\xi\eta}\cos\varphi,\quad y = 2\sqrt{\xi\eta}\sin\varphi,\quad z=\xi-\eta,$$

$$2\xi = r+z,\quad 2\eta = r-z,\quad \varphi = \arctan\frac{y}{x}.$$

Equation (5.24) is more convenient than (5.21) for the calculation of the Laplace operator in parabolic coordinates.

5.4 Show that the Christoffel symbols (5.22) can also be expressed in terms of the metric and inverse metric components,

$$\Gamma^{\gamma}{}_{\beta\alpha} = \frac{1}{2} g^{\gamma\delta} \left(\partial_\beta g_{\delta\alpha} + \partial_\alpha g_{\delta\beta} - \partial_\delta g_{\alpha\beta} \right). \tag{5.36}$$

5.5 Prove the following statement: The Euler-Lagrange equation (see Appendix A, in particular equation (A.3))

$$\frac{d}{d\tau} \frac{\partial L}{\partial \dot{\xi}^\alpha} - \frac{\partial L}{\partial \xi^\alpha} = 0$$

for the Lagrange function

$$L(\xi, \dot{\xi}) = \frac{1}{2} g_{\alpha\beta}(\xi(\tau)) \dot{\xi}^\alpha(\tau) \dot{\xi}^\beta(\tau) \tag{5.37}$$

yields the equation

$$\ddot{\xi}^\alpha(\tau) + \Gamma^\alpha{}_{\beta\gamma}(\xi(\tau)) \dot{\xi}^\beta(\tau) \dot{\xi}^\gamma(\tau) = 0. \tag{5.38}$$

This is a most useful lemma for the calculation of Christoffel symbols. For given metric $g_{\alpha\beta}(\boldsymbol{\xi})$, one simply calculates the Euler-Lagrange equations for the Lagrange function (5.37) and then reads off the Christoffel symbols from the quadratic terms in the velocities $\dot{\xi}(\tau)$.
Equation (5.38) is known as the geodesic equation, because in a general space it yields lines $\xi(\tau)$ of stationary length (e.g. shortest or longest lines). In the flat spaces that we are dealing with in this book, equation (5.38) is the condition for a straight line in terms of the curvilinear coordinates ξ^α.

5.6 Find the eigenvalues and eigenfunctions of the two-dimensional differential operator $H_{x,y} = y\partial_x^2 - \mathrm{i}\partial_y$.

Chapter 6

Harmonic Oscillators and Coherent States

The harmonic oscillator is the general approximation for the dynamics of small fluctuations around a minimum of a potential. This is the reason why harmonic oscillators are very important model systems both in mechanics and in quantum mechanics. In addition there is another reason why we have to discuss the quantum harmonic oscillator in detail. For the discussion of quantum mechanical reactions between particles later on, we have to go beyond ordinary quantum mechanics and use a technique called second quantization or canonical quantum field theory. The techniques of second quantization are based on linear superpositions of infinitely many oscillators. Therefore it is important to have a very good understanding of oscillator eigenstates and of the calculational techniques involved with oscillation operators.

6.1 Basic aspects of harmonic oscillators

The classical motion of a particle in the three-dimensional isotropic potential

$$V(\boldsymbol{x}) = \frac{m}{2}\omega^2 \boldsymbol{x}^2$$

without external driving forces is described by the classical solution

$$\boldsymbol{x}(t) = \boldsymbol{X}\cos(\omega t) + \frac{\boldsymbol{P}}{m\omega}\sin(\omega t),$$

where $\boldsymbol{X} = \boldsymbol{x}(0)$, $\boldsymbol{P} = m\dot{\boldsymbol{x}}(0)$ are the values of location and momentum of the particle at time $t = 0$.
The corresponding Schrödinger equation is

$$\mathrm{i}\hbar\frac{d}{dt}|\psi(t)\rangle = \left(\frac{\mathbf{p}^2}{2m} + \frac{m}{2}\omega^2\mathbf{x}^2\right)|\psi(t)\rangle$$

or after subsitution of energy-time Fourier transformation (5.10),

$$E|\psi(E)\rangle = \left(\frac{\mathbf{p}^2}{2m} + \frac{m}{2}\omega^2\mathbf{x}^2\right)|\psi(E)\rangle. \tag{6.1}$$

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The corresponding differential equation in $\boldsymbol{x}$ representation

$$E\langle \boldsymbol{x}|\psi(E)\rangle = \left(-\frac{\hbar^2}{2m}\Delta + \frac{m}{2}\omega^2\boldsymbol{x}^2\right)\langle \boldsymbol{x}|\psi(E)\rangle$$

can be decomposed into three one-dimensional problems through separation of the spatial variables. The separation ansatz

$$\langle \boldsymbol{x}|\psi(E)\rangle = \prod_{i=1}^{3}\langle x_i|\psi_i(E_i)\rangle$$

yields

$$E = \sum_{i=1}^{3} E_i,$$

where the three energy values E_i and wave functions $\langle x_i|\psi(E_i)\rangle$ have to satisfy the one-dimensional equation

$$E\langle x|\psi(E)\rangle = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\langle x|\psi(E)\rangle + \frac{m}{2}\omega^2x^2\langle x|\psi(E)\rangle. \tag{6.2}$$

6.2 Solution of the harmonic oscillator by the operator method

The one-dimensional oscillator equation (6.2) is in representation free notation

$$E|\psi(E)\rangle = \left(\frac{\mathrm{p}^2}{2m} + \frac{m}{2}\omega^2\mathrm{x}^2\right)|\psi(E)\rangle. \tag{6.3}$$

There exists a very powerful and elegant method to solve equation (6.3) through a transformation from the self-adjoint operators x and p to mutually adjoint operators a and a^+. The substitutions

$$a = \frac{1}{\sqrt{2\hbar}}\left(\sqrt{m\omega}\mathrm{x} + \mathrm{i}\frac{\mathrm{p}}{\sqrt{m\omega}}\right), \quad a^+ = \frac{1}{\sqrt{2\hbar}}\left(\sqrt{m\omega}\mathrm{x} - \mathrm{i}\frac{\mathrm{p}}{\sqrt{m\omega}}\right), \tag{6.4}$$

yield the commutation relation

$$[a, a^+] = 1, \tag{6.5}$$

the inverse transformation

$$\mathrm{x} = \sqrt{\frac{\hbar}{2m\omega}}\,(a + a^+), \quad \mathrm{p} = -\mathrm{i}\sqrt{\frac{m\omega\hbar}{2}}\,(a - a^+), \tag{6.6}$$

and the Hamiltonian in the form

$$H = \frac{1}{2}\hbar\omega(aa^+ + a^+a) = \hbar\omega\left(a^+a + \frac{1}{2}\right).$$

The equations

$$[H, a] = -\hbar\omega a, \quad [H, a^+] = \hbar\omega a^+ \tag{6.7}$$

and

$$H|\psi(E)\rangle = E|\psi(E)\rangle, \tag{6.8}$$

imply that the operator a decreases energy eigenvalues and the operator a^+ increases energy eigenvalues in units of $\hbar\omega$,

$$Ha|\psi(E)\rangle = (E - \hbar\omega)a|\psi(E)\rangle, \quad Ha^+|\psi(E)\rangle = (E + \hbar\omega)a^+|\psi(E)\rangle. \tag{6.9}$$

The operator a is therefore denoted as an *annihilation operator* or *lowering operator*, while a^+ is a *creation operator* or a *raising operator*.
Stability of the system requires existence of a lowest energy state $|\Omega\rangle$. This state must be annihilated by the operator a since otherwise $a|\Omega\rangle$ would be a state of lower energy,

$$\exists|\Omega\rangle\colon\ a|\Omega\rangle = 0, \ \Rightarrow \ H|\Omega\rangle = \frac{1}{2}\hbar\omega|\Omega\rangle.$$

The standard notation for this lowest energy state or vacuum state is $|\Omega\rangle = |0\rangle$. The excited energy eigenstates are then

$$|n\rangle = \frac{(a^+)^n}{\sqrt{n!}}|0\rangle, \tag{6.10}$$

and the corresponding energy eigenvalues follow from

$$H|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle$$

as

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right).$$

These relations are equivalent to

$$a^+a|n\rangle = n|n\rangle,$$

and therefore a^+a returns the level number of a state. The operator a^+a is denoted as an *occupation number operator*, or *number operator* for short, because this operator enumerates how many energy quanta $\hbar\omega$ are contained in an energy level.
For an explanation of the normalization of the states (6.10), we note that

$$\begin{aligned}\langle 0|a^n(a^+)^n|0\rangle &= \langle 0|a^{n-1}[a, (a^+)^n]|0\rangle = n\langle 0|a^{n-1}(a^+)^{n-1}|0\rangle \\ &= n!\langle 0|0\rangle = n!,\end{aligned} \tag{6.11}$$

where

$$[a, (a^+)^n] = n(a^+)^{n-1}$$

is easily proved by induction (and the proof (6.11) on a more formal level would also involve an induction step).
We have for arbitrary states $|\psi\rangle$

$$\langle 0|a^+|\psi\rangle = (\langle\psi|a|0\rangle)^+ = 0$$

and therefore the projector $\langle 0|a^+$ annihilates every state,

$$\langle 0|a^+ = 0.$$

6.3 Construction of the states in the x-representation

We construct the expansion coefficients $\langle x|n\rangle$ of the states with respect to the $|x\rangle$-basis. In the first step we construct the components $\langle x|0\rangle$ of the ground state $|0\rangle$. The equation $a|0\rangle = 0$ in x representation,

$$\langle x|a|0\rangle = \left(\sqrt{\frac{m\omega}{2\hbar}}x + \sqrt{\frac{\hbar}{2m\omega}}\frac{d}{dx}\right)\langle x|0\rangle = 0,$$

yields

$$\langle x|0\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} \exp\left(-\frac{m\omega}{2\hbar}x^2\right),$$

and from this the x-components of the higher states can be calculated in the following way:

$$\begin{aligned}\langle x|n\rangle &= \frac{1}{\sqrt{n!}}\langle x|(a^+)^n|0\rangle \\ &= \frac{1}{\sqrt{n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\left(\sqrt{\frac{m\omega}{2\hbar}}x - \sqrt{\frac{\hbar}{2m\omega}}\frac{d}{dx}\right)^n \exp\left(-\frac{m\omega}{2\hbar}x^2\right) \\ &= \frac{1}{\sqrt{2^n n!}}\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)\exp\left(-\frac{m\omega}{2\hbar}x^2\right). \qquad (6.12)\end{aligned}$$

The functions $H_n(x)$ are the Hermite polynomials

$$H_n(x) = \exp\left(\frac{1}{2}x^2\right)\left(x - \frac{d}{dx}\right)^n \exp\left(-\frac{1}{2}x^2\right), \qquad (6.13)$$

$$H_0(x) = 1, \quad H_1(x) = 2x, \quad H_2(x) = 4x^2 - 2, \ldots$$

Properties of Hermite polynomials are discussed in Appendix D.

The general state of the one-dimensional harmonic oscillator in the x-representation is

$$\langle x|\psi(t)\rangle = \sum_{n\geq 0}\langle x|n\rangle\langle n|\psi(t)\rangle = \sum_{n\geq 0}\langle x|n\rangle\langle n|\psi(0)\rangle \exp\left(-\mathrm{i}\left(n+\frac{1}{2}\right)\omega t\right),$$

and the general normalizable state of a 1-dimensional system with Hamiltonian H (here $\dot{H}=0$) in the x-representation can be expanded in oscillator eigenstates

$$\begin{aligned}\langle x|\psi(t)\rangle &= \sum_{n\geq 0}\langle x|n\rangle\langle n|\psi(t)\rangle = \sum_{n\geq 0}\langle x|n\rangle\langle n|\exp(-\mathrm{i}Ht/\hbar)|\psi(0)\rangle \\ &= \sum_{n\geq 0}\langle x|\exp(-\mathrm{i}Ht/\hbar)|n\rangle\langle n|\psi(0)\rangle.\end{aligned}$$

These expansions are particular examples of the completeness relations of Sturm-Liouville eigenfunctions discussed in Appendix C. They hold pointwise for every continuous square integrable function $\langle x|\psi(t)\rangle$, and they hold for the derivatives as long as the derivatives are continuous (otherwise they remain valid in the mean).

Oscillator eigenstates in k space and bilinear relations for Hermite polynomials

The k space representations of the oscillator energy eigenstates can be constructed in the same way as the x representations. The equation

$$\langle k|a|0\rangle = \mathrm{i}\left(\sqrt{\frac{m\omega}{2\hbar}}\frac{d}{dk}+\sqrt{\frac{\hbar}{2m\omega}}k\right)\langle k|0\rangle = 0$$

yields

$$\langle k|0\rangle = \left(\frac{\hbar}{\pi m\omega}\right)^{\frac{1}{4}}\exp\left(-\frac{\hbar}{2m\omega}k^2\right),$$

and from this the k-components of the higher states can be calculated,

$$\begin{aligned}\langle k|n\rangle &= \frac{1}{\sqrt{n!}}\langle k|(a^+)^n|0\rangle \\ &= \frac{\mathrm{i}^n}{\sqrt{n!}}\left(\frac{\hbar}{\pi m\omega}\right)^{\frac{1}{4}}\left(\sqrt{\frac{m\omega}{2\hbar}}\frac{d}{dk}-\sqrt{\frac{\hbar}{2m\omega}}k\right)^n\exp\left(-\frac{\hbar}{2m\omega}k^2\right) \\ &= \frac{(-\mathrm{i})^n}{\sqrt{2^n n!}}\left(\frac{\hbar}{\pi m\omega}\right)^{\frac{1}{4}}H_n\left(\sqrt{\frac{\hbar}{m\omega}}k\right)\exp\left(-\frac{\hbar}{2m\omega}k^2\right).\end{aligned}$$

From this and the previous result we find an expression for the decomposition of plane waves,

$$\langle x|k\rangle = \frac{1}{\sqrt{2\pi}}\exp(\mathrm{i}kx) = \frac{1}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{\mathrm{i}^n}{2^n n!}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)H_n\left(\sqrt{\frac{\hbar}{m\omega}}k\right) \times \exp\left[-\frac{1}{\hbar\omega}\left(\frac{\hbar^2k^2}{2m}+\frac{m}{2}\omega^2x^2\right)\right]. \tag{6.14}$$

This reads in scaled variables

$$\frac{1}{\sqrt{2\pi}}\exp(\mathrm{i}KX) = \frac{1}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{\mathrm{i}^n}{2^n n!}H_n(X)\,H_n(K)\exp\left(-\frac{1}{2}\left(K^2+X^2\right)\right).$$

This equation follows from the Mehler formula (D.8) in the limit $z \to \mathrm{i}$.
For comparison, we must also have

$$\langle x|y\rangle = \delta(x-y) = \sqrt{\frac{m\omega}{\pi\hbar}}\sum_{n=0}^{\infty}\frac{1}{2^n n!}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)H_n\left(\sqrt{\frac{m\omega}{\hbar}}y\right) \times \exp\left(-\frac{m\omega}{2\hbar}\left(x^2+y^2\right)\right), \tag{6.15}$$

or in scaled variables

$$\delta(X-Y) = \frac{1}{\sqrt{\pi}}\sum_{n=0}^{\infty}\frac{1}{2^n n!}H_n(X)\,H_n(Y)\exp\left(-\frac{1}{2}\left(X^2+Y^2\right)\right).$$

This equation follows from the Mehler formula (D.8) in the limit $z \to 1$ and using $\lim_{\kappa\to\infty}\kappa\exp(-\kappa^2x^2) = \sqrt{\pi}\delta(x)$.

6.4 Lemmata for exponentials of operators

Exponentials $\exp(A)$ of operators appear in many applications of quantum mechanics, because

• exponentials of Hamiltonians generate time evolution in quantum systems (time evolution operators),

• exponentials of operators generate continuous transformations (e.g. translations or rotations or phase rotations etc.) in quantum systems, and because

• the exponential $\exp(A)$ shifts the eigenvalues of the complementary operator A_c (where $[A, A_c] = const.$), i.e. $\exp(A)$ maps one eigenstate of A_c into another eigenstate. In this case the exponential operator is also denoted as a *shift operator*.

There are three very useful theorems for products involving operator exponentials. The first one is

Lemma 1:

$$\exp(A)B\exp(-A) = \sum_{n\geq 0} \frac{1}{n!} \overset{n}{[}A, B]. \tag{6.16}$$

The proof simply proceeds by Taylor expansion of $\exp(\lambda A)B\exp(-\lambda A)$ with respect to λ.
The second useful lemma requires that all higher order commutators of two operators A and B vanish:

$$\overset{2}{[}A, B] = 0, \ \overset{2}{[}B, A] = 0. \tag{6.17}$$

Then the following equation holds[1],

Lemma 2: If equations (6.17) hold, then

$$\exp(A)\exp(B) = \exp\left(A + B + \frac{1}{2}[A, B]\right). \tag{6.18}$$

Proof: We will prove (6.18) in the equivalent form

$$\exp(\lambda A)\exp(\lambda B) = \exp\left(\lambda A + \lambda B + \frac{\lambda^2}{2}[A, B]\right). \tag{6.19}$$

This equation is certainly correct for $\lambda = 0$. For the first order derivative of the left hand side of equation (6.19) one finds with (6.16) and (6.17)

$$\begin{aligned}\frac{d}{d\lambda}\exp(\lambda A)\exp(\lambda B) &= (A + B + \lambda[A, B])\exp(\lambda A)\exp(\lambda B)\\ &= \exp(\lambda A)\exp(\lambda B)(A + B + \lambda[A, B]),\end{aligned}$$

while the first order derivative of the right hand side of (6.19) is

$$\begin{aligned}\frac{d}{d\lambda}\exp\left(\lambda A + \lambda B + \frac{\lambda^2}{2}[A, B]\right) &= (A + B + \lambda[A, B])\\ &\quad \times \exp\left(\lambda A + \lambda B + \frac{\lambda^2}{2}[A, B]\right)\\ &= \exp\left(\lambda A + \lambda B + \frac{\lambda^2}{2}[A, B]\right)\\ &\quad \times (A + B + \lambda[A, B]).\end{aligned} \tag{6.20}$$

Therefore we also have

$$\begin{aligned}\left[\frac{d}{d\lambda}\exp(\lambda A)\exp(\lambda B)\right]_{\lambda=0} &= A + B\\ &= \left[\frac{d}{d\lambda}\exp\left(\lambda A + \lambda B + \frac{\lambda^2}{2}[A, B]\right)\right]_{\lambda=0}.\end{aligned} \tag{6.21}$$

[1]There is a generalization of equation (6.18) known as the Baker-Campbell-Hausdorff formula, which holds if the higher order commutators of A and B do not vanish. The recursive construction of higher order terms is outlined in Appendix E.

Equations (6.20,6.20,6.21) then also yield that in general

$$F_n \equiv \left[\frac{d^n}{d\lambda^n}\exp(\lambda A)\exp(\lambda B)\right]_{\lambda=0} = \left[\frac{d^n}{d\lambda^n}\exp\left(\lambda A+\lambda B+\frac{\lambda^2}{2}[A,B]\right)\right]_{\lambda=0}$$

by induction:

$$\begin{aligned}
F_{n+1} &= \left[\frac{d^{n+1}}{d\lambda^{n+1}}\exp(\lambda A)\exp(\lambda B)\right]_{\lambda=0}\\
&= \left[\frac{d^n}{d\lambda^n}\left(A+B+\lambda[A,B]\right)\exp(\lambda A)\exp(\lambda B)\right]_{\lambda=0}\\
&= (A+B)\left[\frac{d^n}{d\lambda^n}\exp(\lambda A)\exp(\lambda B)\right]_{\lambda=0}\\
&\quad + n[A,B]\left[\frac{d^{n-1}}{d\lambda^{n-1}}\exp(\lambda A)\exp(\lambda B)\right]_{\lambda=0}\\
&= (A+B)\left[\frac{d^n}{d\lambda^n}\exp\left(\lambda A+\lambda B+\frac{\lambda^2}{2}[A,B]\right)\right]_{\lambda=0}\\
&\quad + n[A,B]\left[\frac{d^{n-1}}{d\lambda^{n-1}}\exp\left(\lambda A+\lambda B+\frac{\lambda^2}{2}[A,B]\right)\right]_{\lambda=0}\\
&= \left[\frac{d^n}{d\lambda^n}\left(A+B+\lambda[A,B]\right)\exp\left(\lambda A+\lambda B+\frac{\lambda^2}{2}[A,B]\right)\right]_{\lambda=0}\\
&= \left[\frac{d^{n+1}}{d\lambda^{n+1}}\exp\left(\lambda A+\lambda B+\frac{\lambda^2}{2}[A,B]\right)\right]_{\lambda=0}.
\end{aligned}$$

Therefore the two operators have the same expansion in λ, and since they also agree for $\lambda = 0$ they must be the same.
The third lemma is useful to combine certain products of three operator exponentials.

Lemma 3:

$$\exp(A)\exp(B)\exp(-A) = \exp[\exp(A)B\exp(-A)] \tag{6.22}$$

The proof proceeds by applying the Taylor expansion $\exp(C) = \sum_{n=0}^{\infty} C^n/n!$ for $C = \exp(A)B\exp(-A)$.
The exponent on the right hand side of Lemma 3 can be evaluated with Lemma 1. We will often use these *lemmata* in quantum mechanical calculations.

6.5 Coherent states

Coherent states were introduced by Schrödinger in 1926 as quantum states which reproduce the classical oscillatory motion of a harmonic oscillator on the level of expectation values[2].

[2] E. Schrödinger, Naturwissenschaften 14, 664 (1926).

Equation (6.16) implies

$$\exp(-\lambda a^+) a \exp(\lambda a^+) = a + \lambda,$$

and therefore

$$a \exp(\lambda a^+)|0\rangle = \exp(\lambda a^+)(a + \lambda)|0\rangle = \lambda \exp(\lambda a^+)|0\rangle,$$

i.e. the state $\exp(\lambda a^+)|0\rangle$ is an eigenstate of the annihilation operator a with eigenvalue λ. It is not yet normalized, however. We can remedy this by replacing the shift operator $\exp(\lambda a^+)$ by a unitary shift operator with the same effect on a,

$$\exp(\lambda^+ a - \lambda a^+) a \exp(\lambda a^+ - \lambda^+ a) = a + \lambda,$$

and therefore the normalized eigenstate of a is

$$|\lambda\rangle = \exp(\lambda a^+ - \lambda^+ a)|0\rangle = \exp\left(-\frac{1}{2}|\lambda|^2\right) \exp(\lambda a^+)|0\rangle$$
$$= \exp\left(-\frac{1}{2}|\lambda|^2\right) \sum_{n=0}^{\infty} \frac{\lambda^n}{\sqrt{n!}}|n\rangle.$$

Here we used Lemma 2,

$$\exp(\lambda a^+) \exp(-\lambda^+ a) = \exp\left(\lambda a^+ - \lambda^+ a + \frac{1}{2}|\lambda|^2\right)$$
$$= \exp(\lambda a^+ - \lambda^+ a) \exp\left(\frac{1}{2}|\lambda|^2\right).$$

We also used an implicit convention that a state $|n\rangle$ labelled by an integer is an eigenstate of the Hamiltonian H of the harmonic oscillator, while a state $|\lambda\rangle$ labelled by a complex number is an eigenstate of a. Only the lowest energy state $|0\rangle$ is an eigenstate of both operators.

The states $|\lambda\rangle$ for $\lambda \neq 0$ are apparently superpositions of all energy eigenstates, and they are known as coherent states. They can be used to generate quantum states which move like a classical particle in the oscillator potential.

Classical motion with initial values $x(0) = X$ and $p(0) = P$ is described by

$$x_{cl}(t) = X \cos(\omega t) + \frac{P}{m\omega} \sin(\omega t),$$
$$p_{cl}(t) = P \cos(\omega t) - m\omega X \sin(\omega t), \tag{6.23}$$

and what we want to have is a state $|\lambda(t)\rangle$ with exactly these time dependences of its expectation values,

$$\langle\lambda(t)|x|\lambda(t)\rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle\lambda(t)|a + a^+|\lambda(t)\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left[\lambda(t) + \lambda^+(t)\right]$$
$$= x_{cl}(t) = X \cos(\omega t) + \frac{P}{m\omega} \sin(\omega t),$$
$$\langle\lambda(t)|p|\lambda(t)\rangle = -i\sqrt{\frac{m\omega\hbar}{2}}\langle\lambda(t)|a - a^+|\lambda(t)\rangle = -i\sqrt{\frac{m\omega\hbar}{2}}\left[\lambda(t) - \lambda^+(t)\right]$$
$$= p_{cl}(t) = P \cos(\omega t) - m\omega X \sin(\omega t).$$

This yields

$$\begin{aligned}\lambda(t) &= \sqrt{\frac{m\omega}{2\hbar}}x_{cl}(t) + \mathrm{i}\frac{p_{cl}(t)}{\sqrt{2m\omega\hbar}} \\ &= \left(\sqrt{\frac{m\omega}{2\hbar}}X + \mathrm{i}\frac{P}{\sqrt{2m\omega\hbar}}\right)\exp(-\mathrm{i}\omega t). \end{aligned} \tag{6.24}$$

We can also write the coherent state in terms of the operators x and p,

$$|\lambda(t)\rangle = \exp\left[\lambda(t)a^+ - \lambda^+(t)a\right]|0\rangle = \exp\left(\frac{\mathrm{i}}{\hbar}\left[p_{cl}(t)x - x_{cl}(t)p\right]\right)|0\rangle. \tag{6.25}$$

We still have to show that the coherent states (6.25) satisfy the Schrödinger equation for the harmonic oscillator. We have with $|\lambda|^2(t) = |\lambda|^2$ time-independent,

$$\begin{aligned}\mathrm{i}\hbar\frac{d}{dt}|\lambda(t)\rangle &= \mathrm{i}\hbar\dot{\lambda}(t)a^+|\lambda(t)\rangle = \hbar\omega\lambda(t)a^+|\lambda(t)\rangle = \hbar\omega a^+ a|\lambda(t)\rangle \\ &= H|\lambda(t)\rangle - \frac{1}{2}\hbar\omega|\lambda(t)\rangle.\end{aligned}$$

Therefore the oscillating state which satisfies the Schrödinger equation of the harmonic oscillator including the zero point energy term is $|\lambda(t)\rangle\exp(-\mathrm{i}\omega t/2)$. For the x representation of the coherent states, we notice

$$\begin{aligned}\langle x|\lambda(t)\rangle &= \exp\left(-\frac{1}{2}|\lambda(t)|^2\right)\langle x|\exp\left(\lambda(t)a^+\right)|0\rangle \\ &= \exp\left(-\frac{1}{2}|\lambda(t)|^2\right)\langle x|\exp\left[\frac{\lambda(t)}{\sqrt{2\hbar}}\left(\sqrt{m\omega}x - \mathrm{i}\frac{p}{\sqrt{m\omega}}\right)\right]|0\rangle \\ &= \exp\left(\lambda(t)\sqrt{\frac{m\omega}{2\hbar}}x\right)\exp\left(-\frac{1}{2}|\lambda(t)|^2 - \frac{1}{4}\lambda^2(t)\right) \\ &\quad\times\langle x|\exp\left(-\mathrm{i}\lambda(t)\frac{p}{\sqrt{2m\omega\hbar}}\right)|0\rangle \\ &= \exp\left(\lambda(t)\sqrt{\frac{m\omega}{2\hbar}}x\right)\exp\left(-\frac{1}{2}|\lambda(t)|^2 - \frac{1}{4}\lambda^2(t)\right) \\ &\quad\times\langle x - \lambda(t)\sqrt{\frac{\hbar}{2m\omega}}|0\rangle \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\exp\left(\lambda(t)\sqrt{\frac{m\omega}{2\hbar}}x\right)\exp\left(-\frac{1}{2}|\lambda(t)|^2 - \frac{1}{4}\lambda^2(t)\right) \\ &\quad\times\exp\left(-\frac{m\omega}{2\hbar}x^2 + \sqrt{\frac{m\omega}{2\hbar}}\lambda(t)x - \frac{1}{4}\lambda^2(t)\right) \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\exp\left(-\frac{m\omega}{2\hbar}x^2 + \sqrt{\frac{2m\omega}{\hbar}}\lambda(t)x - \frac{1}{2}|\lambda(t)|^2 - \frac{1}{2}\lambda^2(t)\right).\end{aligned}$$

This yields with

$$\begin{aligned}\frac{1}{2}|\lambda(t)|^2+\frac{1}{2}\lambda^2(t) &= \frac{m\omega}{2\hbar}\left(X\cos(\omega t)+\frac{P}{m\omega}\sin(\omega t)\right)^2\\ &\quad +\mathrm{i}\frac{m\omega}{2\hbar}\left(X\cos(\omega t)+\frac{P}{m\omega}\sin(\omega t)\right)\\ &\quad \times\left(\frac{P}{m\omega}\cos(\omega t)-X\sin(\omega t)\right)\\ &= \frac{m\omega}{2\hbar}x_{cl}^2(t)+\mathrm{i}\frac{x_{cl}(t)p_{cl}(t)}{2\hbar}\end{aligned}$$

the result

$$\langle x|\lambda(t)\rangle=\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}\exp\left(-\frac{m\omega}{2\hbar}\left(x-x_{cl}(t)\right)^2+\mathrm{i}\frac{xp_{cl}(t)}{\hbar}-\mathrm{i}\frac{x_{cl}(t)p_{cl}(t)}{2\hbar}\right). \tag{6.26}$$

Comparison of equation (6.26) with equations (5.5) and (5.6) or direct evaluation yields the momentum representation of the coherent states,

$$\langle p|\lambda(t)\rangle=\frac{1}{(\pi m\omega\hbar)^{\frac{1}{4}}}\exp\left(-\frac{\left(p-p_{cl}(t)\right)^2}{2m\omega\hbar}-\mathrm{i}\frac{x_{cl}(t)p}{\hbar}+\mathrm{i}\frac{x_{cl}(t)p_{cl}(t)}{2\hbar}\right). \tag{6.27}$$

The variances of the expectation values $\langle x\rangle(t)=x_{cl}(t)$ and $\langle p\rangle(t)=p_{cl}(t)$ of the coherent state $|\lambda(t)\rangle$ (6.24,6.25) are

$$\Delta x^2=\frac{\hbar}{2m\omega},\quad \Delta p^2=\frac{m\omega\hbar}{2}. \tag{6.28}$$

In terms of the force constant $K=m\omega^2$ of the harmonic potential the width of the coherent states is $\Delta x^2\propto 1/\sqrt{mK}$. This equation holds with an n-dependent factor also for the energy eigenstates $|n\rangle$, see Problem 2. We have seen in Section 3.4 that the kinetic term $p^2/2m$ drives wave packets apart. The attractive potential $V(x)=Kx^2/2$ on the other hand tries to collapse wave packets, and the balance of these terms yields the stable wave packets (6.12) and (6.24,6.25). This is consistent with $\Delta x^2\propto 1/\sqrt{mK}$, because $mK\to\infty$ would correspond to domination of the attractive potential while $mK\to 0$ would imply domination of the kinetic term. In the next chapter we will see that the same basic mechanism also stabilizes the bound states of atoms. Balance between kinetic terms driving wave packets apart and the attractive Coulomb potential trying to contract the wave function generates minimal possible sizes of wave functions for given kinetic parameters $1/m$ and force constants Ze^2, thus preventing electrons from the classically inevitable core collapse.

Scalar products and overcompleteness of coherent states

We have

$$\begin{aligned}\langle\lambda|\mu\rangle &= \exp\left(-\frac{1}{2}\left(|\lambda|^2+|\mu|^2\right)\right)\sum_{n=0}^{\infty}\frac{(\lambda^+\mu)^n}{n!}\\ &= \exp\left(\lambda^+\mu-\frac{1}{2}\left(|\lambda|^2+|\mu|^2\right)\right)\end{aligned} \tag{6.29}$$

and

$$|\langle\lambda|\mu\rangle|^2 = \exp\bigl(-|\lambda-\mu|^2\bigr),$$

i.e. coherent states are never orthogonal. Therefore any completeness relation cannot be unique, and coherent states are overcomplete. One can still identify a kind of "canonical" completeness relation in which all coherent states contribute with the same weight. We use

$$dz = \exp(\mathrm{i}\varphi)dr + \mathrm{i}z d\varphi, \quad \frac{d\overline{z}\wedge dz}{2\mathrm{i}} = d\Re z\wedge d\Im z = dr\wedge d\varphi\, r$$

to find the particular completeness relation

$$\begin{aligned}\int\frac{d\overline{z}\wedge dz}{2\pi\mathrm{i}}|z\rangle\langle z| &= \int\frac{d\overline{z}\wedge dz}{2\pi\mathrm{i}}\exp\bigl(-|z|^2\bigr)\sum_{m,n}|m\rangle\frac{z^m\overline{z}^n}{\sqrt{m!n!}}\langle n|\\ &= \frac{1}{\pi}\int_0^{\infty}dr\int_0^{2\pi}d\varphi\,\exp\bigl(-r^2\bigr)\sum_{m,n}|m\rangle\frac{r^{m+n+1}}{\sqrt{m!n!}}\\ &\quad\times\exp[\mathrm{i}(n-m)\varphi]\,\langle n|\\ &= 2\int_0^{\infty}dr\,r\exp\bigl(-r^2\bigr)\sum_n|n\rangle\frac{r^{2n}}{n!}\langle n|\\ &= \sum_n\int_0^{\infty}du\left(-\frac{d}{d\alpha}\right)^n\exp(-\alpha u)\Big|_{\alpha=1}\frac{1}{n!}|n\rangle\langle n|\\ &= \sum_n\left(-\frac{d}{d\alpha}\right)^n\frac{1}{\alpha}\Big|_{\alpha=1}\frac{1}{n!}|n\rangle\langle n| = \sum_n|n\rangle\langle n| = 1.\end{aligned}$$

For example, substitution of

$$\langle z|n\rangle = \frac{\overline{z}^n}{\sqrt{n!}}\exp\left(-\frac{1}{2}|z|^2\right)$$

yields the following decomposition of the energy eigenstates of the harmonic oscillator in terms of coherent states,

$$|n\rangle = \int\frac{d\overline{z}\wedge dz}{2\pi\mathrm{i}}|z\rangle\frac{\overline{z}^n}{\sqrt{n!}}\exp\left(-\frac{1}{2}|z|^2\right).$$

Inserting equation (6.29) yields a decomposition of coherent states in terms of coherent states,

$$|\zeta\rangle = \int \frac{d\overline{z} \wedge dz}{2\pi \mathrm{i}} |z\rangle \exp\left(\overline{z}\zeta - \frac{1}{2}\left(|z|^2 + |\zeta|^2\right)\right).$$

Note that for the coherent state parameter $\lambda(t)$ (6.24)

$$\frac{d\overline{\lambda}(t) \wedge d\lambda(t)}{2\pi \mathrm{i}} = \frac{dx_{cl}(t) \wedge dp_{cl}(t)}{h} = \frac{dX \wedge dP}{h},$$

or if we denote the classical parameters simply with x and p,

$$\int \frac{dx \wedge dp}{h} |\lambda_{x,p}(t)\rangle\langle\lambda_{x,p}(t)| = 1.$$

Later we will encounter the measure $dx \wedge dp/h$ in phase space also in the density of states.

Squeezed states

We try to construct new oscillation operators b, b^+ from the oscillation operators (6.4). Substitution of the linear *ansatz*

$$b = Aa + Ba^+, \quad b^+ = \overline{A}a^+ + \overline{B}a$$

into the condition $[b, b^+] = 1$ yields

$$|A|^2 - |B|^2 = 1,$$

i.e. we find

$$b = \exp(\mathrm{i}\alpha)\cosh(u)a + \exp(\mathrm{i}\beta)\sinh(u)a^+,$$

$$b^+ = \exp(-\mathrm{i}\alpha)\cosh(u)a^+ + \exp(-\mathrm{i}\beta)\sinh(u)a.$$

The phase factors are irrelevant in the following. Therefore we study the oscillator operators

$$a(u) = \cosh(u)a + \sinh(u)a^+ = \frac{1}{\sqrt{2\hbar}}\left(\sqrt{m\omega}x\exp(u) + \mathrm{i}\frac{p\exp(-u)}{\sqrt{m\omega}}\right)$$

and

$$a^+(u) = \cosh(u)a^+ + \sinh(u)a = \frac{1}{\sqrt{2\hbar}}\left(\sqrt{m\omega}x\exp(u) - \mathrm{i}\frac{p\exp(-u)}{\sqrt{m\omega}}\right).$$

The x and p operators of the original oscillator are

$$\mathrm{x} = \sqrt{\frac{\hbar}{2m\omega}}\left(a + a^+\right) = \sqrt{\frac{\hbar}{2m\omega}}\exp(-u)\left(a(u) + a^+(u)\right)$$

and

$$\mathrm{p} = -\mathrm{i}\sqrt{\frac{m\omega\hbar}{2}}\left(a - a^+\right) = -\mathrm{i}\sqrt{\frac{m\omega\hbar}{2}}\exp(u)\left(a(u) - a^+(u)\right).$$

We can think of the new operators $a(u)$ and $a^+(u)$ as oscillation operators for a harmonic oscillator with a u-dependent product of mass and frequency,

$$(m\omega)(u) = (m\omega)\exp(2u). \tag{6.30}$$

The coherent state for the new oscillation operators $|\lambda\rangle(u) = \exp(\lambda a^+(u) - \lambda^+ a(u))|0\rangle_u$, $a(u)|0\rangle_u = 0$, has expectation values and variances

$$\langle x\rangle(u) = \sqrt{\frac{\hbar}{2m\omega}}\exp(-u)\left(\lambda + \lambda^+\right) = \langle x\rangle\Big|_{u=0} \times \exp(-u),$$

$$\langle p\rangle(u) = -\mathrm{i}\sqrt{\frac{m\omega\hbar}{2}}\exp(u)\left(\lambda - \lambda^+\right) = \langle p\rangle\Big|_{u=0} \times \exp(u),$$

$$\Delta x^2(u) = \frac{\hbar}{2m\omega}\exp(-2u) = \Delta x^2\Big|_{u=0} \times \exp(-2u),$$

$$\Delta p^2(u) = \frac{m\omega\hbar}{2}\exp(2u) = \Delta p^2\Big|_{u=0} \times \exp(2u),$$

i.e. the uncertainty in x or p direction is squeezed at the expense of a corresponding increase of the uncertainty in the complementary direction.
We could formally write

$$\lambda a^+(u) - \lambda^+ a(u) = \lambda(u)a^+ - \lambda^+(u)a$$

with $\lambda(u) = \lambda\cosh(u) - \lambda^+\sinh(u)$. However, $|0\rangle_u \neq |0\rangle$ and therefore $|\lambda\rangle_u \neq |\lambda(u)\rangle$. Without the change in the vacuum, the variances could not change. For the actual transformation, we note that

$$a(u) = \exp\Big(\frac{u}{2}\big[a^2 - (a^+)^2\big]\Big)\, a \exp\Big(-\frac{u}{2}\big[a^2 - (a^+)^2\big]\Big)$$

and therefore

$$|0\rangle_u = \exp\Big(\frac{u}{2}\big[a^2 - (a^+)^2\big]\Big)|0\rangle, \quad |\lambda\rangle_u = \exp\Big(\frac{u}{2}\big[a^2 - (a^+)^2\big]\Big)|\lambda\rangle.$$

6.6 Problems

6.1 Write down the p-representation of the Schrödinger equation for the one-dimensional harmonic oscillator. Which transformations between the parameters m and ω map the p-representation into the x-representation?

6.2 Calculate the widths Δx_n and Δp_n of the n-th energy eigenstate of the harmonic oscillator.
Remark: This is most conveniently done using the annihilation and creation operators.

6.3 A one-dimensional oscillator at time $t = 0$ is in a state

$$|\psi_\alpha\rangle = \cos\alpha|0\rangle + \exp(\mathrm{i}\varphi)\sin\alpha|1\rangle.$$

6.3a Calculate the expectation values $\langle x\rangle(t)$, $\langle p\rangle(t)$ and $\langle E\rangle$ for the oscillator.
6.3b Calculate the uncertainties $\Delta x(t)$, $\Delta p(t)$ and ΔE for the oscillator.

6.4 For the oscillator from problem 6.3, how large is the probability density to find the oscillator in the location x at time t?

6.5 Show that every coherent state $|\lambda\rangle = \exp(\lambda a^+ - \lambda^+ a)|0\rangle$ has the variances (6.28).

6.6 Calculate the energy expectation value $\langle E\rangle$ and the energy uncertainty ΔE for the coherent state $|\lambda\rangle$. Which values do you get in particular for the state $|\lambda(t)\rangle$ (6.25) which reproduces the classical trajectories (6.23)?

Chapter 7

Central Forces in Quantum Mechanics

Radially symmetric problems appear if the interaction between two particles depends only on their separation r. We will first see how the dynamical problem of the motion of the two particles can be separated in terms of center of mass motion and relative motion and then write the effective Hamiltonian for the relative motion of the two particles in spherical coordinates.

7.1 Separation of center of mass motion and relative motion

The separation of center of mass motion and relative motion proceeds like in classical mechanics. The Hamiltonian of the 2-particle system is

$$H = \frac{\mathbf{p}_1^2}{2m_1} + \frac{\mathbf{p}_2^2}{2m_2} + V(|\mathbf{x}_1 - \mathbf{x}_2|) = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + V(r), \tag{7.1}$$

where

$$M = m_1 + m_2, \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \tag{7.2}$$

are the total and reduced mass,

$$\mathbf{R} = \frac{m_1\mathbf{x}_1 + m_2\mathbf{x}_2}{m_1 + m_2}, \quad \mathbf{r} = \mathbf{x}_1 - \mathbf{x}_2 \tag{7.3}$$

are the operators for center of mass and relative coordinates, and

$$\mathbf{P} = M\dot{\mathbf{R}} = \mathbf{p}_1 + \mathbf{p}_2, \quad \mathbf{p} = \mu\dot{\mathbf{r}} = \frac{\mu}{m_1}\mathbf{p}_1 - \frac{\mu}{m_2}\mathbf{p}_2 = \frac{m_2\mathbf{p}_1 - m_1\mathbf{p}_2}{m_1 + m_2} \tag{7.4}$$

are the momentum operators of center of mass motion and relative motion. The relative motion of the two original particles also comes with an angular momentum

$$\boldsymbol{l} = \mathbf{x}_1 \times \mathbf{p}_1 + \mathbf{x}_2 \times \mathbf{p}_2 - \mathbf{R} \times \mathbf{P} = \mathbf{r} \times \mathbf{p}. \tag{7.5}$$

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The inverse transformations are

$$\mathbf{x}_1 = \mathbf{R} + \frac{m_2}{M}\mathbf{r}, \quad \mathbf{x}_2 = \mathbf{R} - \frac{m_1}{M}\mathbf{r}, \quad \mathbf{p}_1 = \frac{m_1}{M}\mathbf{P} + \mathbf{p}, \quad \mathbf{p}_2 = \frac{m_2}{M}\mathbf{P} - \mathbf{p}, \tag{7.6}$$

and the $\boldsymbol{\nabla}$ operators transform as

$$\frac{\partial}{\partial \boldsymbol{R}} = \frac{\partial}{\partial \boldsymbol{x}_1} + \frac{\partial}{\partial \boldsymbol{x}_2}, \quad \frac{\partial}{\partial \boldsymbol{r}} = \frac{m_2}{M}\frac{\partial}{\partial \boldsymbol{x}_1} - \frac{m_1}{M}\frac{\partial}{\partial \boldsymbol{x}_2},$$

$$\frac{\partial}{\partial \boldsymbol{x}_1} = \frac{m_1}{M}\frac{\partial}{\partial \boldsymbol{R}} + \frac{\partial}{\partial \boldsymbol{r}}, \quad \frac{\partial}{\partial \boldsymbol{x}_1} = \frac{m_2}{M}\frac{\partial}{\partial \boldsymbol{R}} - \frac{\partial}{\partial \boldsymbol{r}}.$$

These are the same transformations for operators as the corresponding transformations for classical coordinates and momenta in classical mechanics. From the quantum mechanics perspective this is not surprising, since the transformation equations for the operators are linear and therefore also hold for the expectation values of the operators, hence for the classical variables. What becomes particularly relevant for quantum mechanics is that the transformations preserve canonical commutation relations,

$$[\mathbf{x}_1, \mathbf{p}_1] = \mathrm{i}\hbar\underline{\mathbf{1}}, \ [\mathbf{x}_2, \mathbf{p}_2] = \mathrm{i}\hbar\underline{\mathbf{1}} \quad \Leftrightarrow \quad [\mathbf{R}, \mathbf{P}] = \mathrm{i}\hbar\underline{\mathbf{1}}, \ [\mathbf{r}, \mathbf{p}] = \mathrm{i}\hbar\underline{\mathbf{1}}.$$

Since the interaction does not depend on the center of mass coordinates, we can separate the center of mass motion in the wave function for the time-independent Schrödinger equation,

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \frac{1}{\sqrt{2\pi}^3} \exp(\mathrm{i}\boldsymbol{K} \cdot \boldsymbol{R})\psi(\boldsymbol{r}), \tag{7.7}$$

and the energy eigenvalue problem $H|\Psi\rangle = E_{\text{total}}|\Psi\rangle$ reduces to an eigenvalue problem for the relative motion

$$E\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2\mu}\Delta\psi(\boldsymbol{r}) + V(r)\psi(\boldsymbol{r}), \tag{7.8}$$

where

$$E_{\text{total}} = E + \frac{\hbar^2 \boldsymbol{K}^2}{2M}$$

is the total energy in the center of mass motion and relative motion.
The discussion of separated solutions in Section 5.5 implies that the solutions for the Hamiltonian (7.1) should have the separated form with respect to center of mass motion and relative motion, $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \Psi(\boldsymbol{R})\psi(\boldsymbol{r})$. However, the reasoning there also implies that we cannot find a solution of the Schrödinger equation which is separated in the actual coordinates of the two particles, $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) \neq \psi_2(\boldsymbol{x}_2)\psi_1(\boldsymbol{x}_1)$. The wave functions of interacting particles are always entangled. This entanglement is easy to understand. Suppose that the

interaction between two particles is attractive and strong enough to generate a bound state between the two particles. If we observe one particle at location $\boldsymbol{x}_1$, we know that the second particle has to be nearby at a location which is determined probabilistically by $|\psi(\boldsymbol{x}_1-\boldsymbol{x}_2)|^2$. On the other hand, if the interaction is weak or repulsive, interactions with other particles will soon dominate each of the two particles, and their two-particle wave function $\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2)=\Psi(\boldsymbol{R})\psi(\boldsymbol{r})$ is not a viable description any more: their mutual entanglement is destroyed by interactions with other particles.

We have based this discussion on the wave function (7.7) which appears in the $(\boldsymbol{x}_1,\boldsymbol{x}_2)$ representation of the time-independent two-particle Schrödinger equation $H|\Psi\rangle = E_{\text{total}}|\Psi\rangle$ with the Hamiltonian (7.1). If one starts from a time-dependent two-particle Schrödinger equation

$$\begin{aligned}\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t) = &-\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial\boldsymbol{x}_1^2}\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t)-\frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial\boldsymbol{x}_2^2}\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t)\\ &+V(|\boldsymbol{x}_1-\boldsymbol{x}_2|)\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t)\end{aligned}$$

the separation *ansatz* for the center of mass motion

$$\begin{aligned}\Psi(\boldsymbol{x}_1,\boldsymbol{x}_2,t) &= \Psi(\boldsymbol{x}_1,\boldsymbol{x}_2)\exp\left(-\mathrm{i}\frac{E_{\text{total}}}{\hbar}t\right)\\ &= \frac{1}{\sqrt{2\pi}^3}\exp\left(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}-\mathrm{i}\frac{\hbar\boldsymbol{K}^2}{2M}t\right)\psi(\boldsymbol{r},t)\\ &= \frac{1}{\sqrt{2\pi}^3}\exp\left(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}-\mathrm{i}\frac{\hbar\boldsymbol{K}^2}{2M}t\right)\psi(\boldsymbol{r})\exp\left(-\mathrm{i}\frac{E}{\hbar}t\right)\end{aligned}$$

leads again to equation (7.8).

Separation of the center of mass motion in the present form works for any potential $V(\boldsymbol{r})$ which only depends on the separation vector $\boldsymbol{r}$ of the two particles. More general, if the 2-particle system moves in a potential of the form

$$V(\boldsymbol{x}_1,\boldsymbol{x}_2)=V(\boldsymbol{r})+W(\boldsymbol{R}),$$

we can separate center of mass motion in the potential $W(\boldsymbol{R})$ from relative motion with the interaction potential $V(\boldsymbol{r})$ and find two independent effective single-particle Schrödinger equations (or Newton equations in mechanics) for the system. An example for this situation would be a hydrogen atom trapped in a potential well, e.g. in ice. If we model the potential well through a three-dimensional oscillator potential, the center of mass motion could be described by oscillator eigenstates $\Psi_{\boldsymbol{N}}(\boldsymbol{R},t)$ while the relative motion between the electron and the proton would be described by the wave functions $\psi_{n,\ell}(r)Y_{\ell,m}(\vartheta,\varphi)\exp(-\mathrm{i}E_nt/\hbar)$ derived in Sections 7.6 and 7.9.

7.2 The concept of symmetry groups

The effective single particle equation (7.8) for relative motion has the same form in every cordinate system which is related to the coordinates $\boldsymbol{r}$ through a rotation $r'^i = R^i{}_a r^a$, or in column vector notation,

$$\boldsymbol{r}' = \underline{R} \cdot \boldsymbol{r}, \quad \underline{R}^T \cdot \underline{R} = \underline{1},$$

cf. Section 4.1 and in particlar equations (4.3) and (4.5). Contrary to Section 4.1, here we use the common left multiplication convention for linear coordinate transformations, $r^a \to r'^i = R^i{}_a r^a$, i.e. our rotation matrix $\underline{R}$ in the present section corresponds to $\underline{R}^T = \underline{R}^{-1}$ in Section 4.1.
Rotations have the following four basic properties:
1. The combination of two rotations $\underline{R}_1$ and $\underline{R}_2$ yields again a rotation $\underline{R}_2 \cdot \underline{R}_1$,

$$\boldsymbol{r}'' = \underline{R}_2 \cdot \boldsymbol{r}' = \underline{R}_2 \cdot (\underline{R}_1 \cdot \boldsymbol{r}) = (\underline{R}_2 \cdot \underline{R}_1) \cdot \boldsymbol{r}.$$

2. The identity transformation $\underline{1}$ is a particular rotation.
3. For every rotation there is an inverse rotation, $\underline{R}^{-1} \cdot \underline{R} = \underline{1}$.
4. Combination of rotations is associative,

$$\underline{R}_3 \cdot (\underline{R}_2 \cdot \underline{R}_1) = (\underline{R}_3 \cdot \underline{R}_2) \cdot \underline{R}_1.$$

These four algebraic properties are common to all sets of symmetry transformations of physical systems, and they have far reaching consequences in the sense that many other interesting properties of symmetry transformations can be derived from these four properties. Every set of mathematical objects having these four properties is therefore denoted as a *group*, and the study of groups is a subdiscipline of algebra denoted as group theory.
Groups which are particularly relevant for quantum mechanics include the following sets:
1. The group of proper rotations is the set of all rotations which does not include inversion of an odd number of axes. Matrices which generate proper rotations do not only satisfy the orthogonality condition

$$\underline{R}^T \cdot \underline{R} = \underline{1},$$

but also the special additional condition

$$\det \underline{R} = 1.$$

The group of proper rotations in three dimensions is therefore also denoted as the *special orthogonal group of rotations in three dimensions*, or SO(3) for short.
2. A group which is closely related to the group SO(3) is the group of unitary 2×2 matrices with determinant 1,

$$\underline{U}^+ \cdot \underline{U} = \underline{1}, \quad \det \underline{U} = 1.$$

This is the *special group of unitary transformations in two dimensions* SU(2).
3. The Poincaré group and its various subgroups, including in particular the proper orthochronous Lorentz group SO(1,3) of proper rotations and Lorentz boosts in Minkowski spacetime, are important for relativistic quantum mechanics.
4. SO(1,3) is closely related to the group of complex 2×2 matrices with determinant 1. This group is often denoted as SL(2,$\mathbb{C}$).
5. Discrete symmetry groups involve e.g. translations along lattice vectors in a regular lattice, or inversions of axes, or rotations by fixed angles. Discrete groups are also important in many applications of quantum mechanics.
6. The known basic particle interactions (besides gravity) are related to the group U(1) of phase transformations, and also to the special unitary groups SU(2) and SU(3).
In this and the following chapter we are primarily concerned with the groups SO(3) and SU(2), and we will develop the relevant aspects of these groups and their matrix representations along the way. Students who would like to acquire a deeper understanding of groups and their representations from a physics perspective should consult the excellent texts by Cornwell [5] for groups in general, or Sexl and Urbantke [35] for emphasis on the Poincaré and Lorentz groups. However, this is not required to understand the following chapters.

7.3 Operators for kinetic energy and angular momentum

The kinetic operator in spherical coordinates follows from (5.23) as

$$\begin{aligned}\frac{\mathbf{p}^2}{2\mu} &= -\frac{\hbar^2}{2\mu}\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\left(\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\frac{\partial^2}{\partial\vartheta^2} + \frac{\cot\vartheta}{r^2}\frac{\partial}{\partial\vartheta} + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)\langle\boldsymbol{r}| \\ &= -\frac{\hbar^2}{2\mu}\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\frac{1}{r}\frac{\partial^2}{\partial r^2}r\langle\boldsymbol{r}| + \frac{\boldsymbol{M}^2}{2\mu r^2},\end{aligned}$$

where $\boldsymbol{M}$ is the angular momentum operator

$$\begin{aligned}\boldsymbol{M} &= \mathbf{x}\times\mathbf{p} = \frac{\hbar}{\mathrm{i}}\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\boldsymbol{r}\times\boldsymbol{\nabla}\langle\boldsymbol{r}| \\ &= \frac{\hbar}{\mathrm{i}}\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\left(\boldsymbol{e}_\varphi\frac{\partial}{\partial\vartheta} - \frac{1}{\sin\vartheta}\boldsymbol{e}_\vartheta\frac{\partial}{\partial\varphi}\right)\langle\boldsymbol{r}| \\ &= \frac{\hbar}{\mathrm{i}}\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\left[\boldsymbol{e}_x\left(-\sin\varphi\frac{\partial}{\partial\vartheta} - \cot\vartheta\cdot\cos\varphi\frac{\partial}{\partial\varphi}\right)\right. \\ &\quad \left. + \boldsymbol{e}_y\left(\cos\varphi\frac{\partial}{\partial\vartheta} - \cot\vartheta\cdot\sin\varphi\frac{\partial}{\partial\varphi}\right) + \boldsymbol{e}_z\frac{\partial}{\partial\varphi}\right]\langle\boldsymbol{r}|. \qquad (7.9)\end{aligned}$$

The property

$$\boldsymbol{M}^2 = -\hbar^2\int d^3\boldsymbol{r}\,|\boldsymbol{r}\rangle\left(\frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)\langle\boldsymbol{r}| \qquad (7.10)$$

follows from

$$\partial_\varphi \boldsymbol{e}_\varphi = -\cos\varphi\, \boldsymbol{e}_x - \sin\varphi\, \boldsymbol{e}_y = -\sin\vartheta\, \boldsymbol{e}_r - \cos\vartheta\, \boldsymbol{e}_\vartheta .$$

The energy eigenvalue problem for the relative motion therefore reads

$$\left(-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2} r + V(r)\right)\langle \boldsymbol{r}|\psi\rangle + \frac{1}{2\mu r^2}\langle \boldsymbol{r}|\boldsymbol{M}^2|\psi\rangle = E\langle \boldsymbol{r}|\psi\rangle, \tag{7.11}$$

and we can deal with the angular part in the equation by first solving the eigenvalue problem for the operator $\boldsymbol{M}^2$.
A useful tool for the analysis of angular momentum operators is the ϵ *tensor* or *Eddington tensor*. The ϵ tensor in an n-dimensional flat space is the completely anti-symmetric tensor of n-th order

$$\epsilon_{i_1 i_2 \ldots i_{k-1} i_k i_{k+1} \ldots i_{m-1} i_m i_{m+1} \ldots i_{n-1} i_n} = -\epsilon_{i_1 i_2 \ldots i_{k-1} i_m i_{k+1} \ldots i_{m-1} i_k i_{m+1} \ldots i_{n-1} i_n}$$

with the normalization

$$\epsilon_{123\ldots n} = 1.$$

The tensor has n^n components. Anti-symmetry and the normalization imply that $n!/2$ of the components have the value 1, $n!/2$ of the components have the value -1, and $n^n - n!$ components vanish. We frequently use the ϵ tensor in three dimensions,

$$\epsilon_{123} = \epsilon_{231} = \epsilon_{312} = -\epsilon_{213} = -\epsilon_{132} = -\epsilon_{321} = 1.$$

A useful identity is

$$\epsilon_{ijk}\epsilon_{k\ell m} = \delta_{i\ell}\delta_{jm} - \delta_{im}\delta_{j\ell}. \tag{7.12}$$

The Cartesian components of the angular momentum operator

$$M_i = \epsilon_{ijk}\mathrm{x}_j \mathrm{p}_k = \frac{\hbar}{\mathrm{i}}\int d^3\boldsymbol{r}|\boldsymbol{r}\rangle \epsilon_{ijk} x_j \frac{\partial}{\partial x^k}\langle \boldsymbol{r}|$$

satisfy the angular momentum commutation relations

$$[M_i, M_j] = \mathrm{i}\hbar\epsilon_{ijk} M_k \tag{7.13}$$

as a consequence of the canonical commutation relations $[\mathrm{x}_i, \mathrm{p}_j] = \mathrm{i}\hbar\delta_{ij}$.
Determination of the eigenvalues of $\boldsymbol{M}^2$ is equivalent to the determination of all hermitian matrix representations of the Lie algebra (7.13), which in turn is equivalent to the determination of all the matrix representations of the rotation group. We will find that all those matrix representations are realized in rotationally symmetric quantum systems. Therefore our next task is the determination of all the matrix representations of (7.13).
We will start the study of matrix representations of the rotation group by looking at the defining representation.

7.4 The defining representation of the three-dimensional rotation group

In Section 4.1 we found the condition

$$\underline{R} \cdot \underline{R}^T = \underline{1}$$

for rotation matrices. This leaves the following possibilities for the matrix[1] $\underline{X} = \ln \underline{R}$,

$$\underline{X}^T = -\underline{X} + 2\pi i n \underline{1}. \tag{7.14}$$

The equation

$$\det(\exp \underline{X}) = \exp(\mathrm{tr}\underline{X}), \tag{7.15}$$

which follows from the existence of a Jordan canonical form (F.2) for every matrix, implies then

$$\det \underline{R} = \exp\left(\mathrm{tr}\frac{\underline{X} + \underline{X}^T}{2}\right) = (-1)^n,$$

i.e $\det \underline{R} = \pm 1$. Pure rotations have $\det \underline{R} = 1$, whereas additional inversion of an odd number of axes[2] yields $\det \underline{R} = -1$. We will focus on pure rotations. The general solution of equation (7.14) in three dimensions and with $n = 0$ is

$$\underline{X} = \begin{pmatrix} 0 & \varphi_3 & -\varphi_2 \\ -\varphi_3 & 0 & \varphi_1 \\ \varphi_2 & -\varphi_1 & 0 \end{pmatrix} = \varphi_i \underline{L}_i = \boldsymbol{\varphi} \cdot \underline{\boldsymbol{L}},$$

where the basis of anti-symmetric real 3×3 matrices

$$\underline{L}_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}, \quad \underline{L}_2 = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \underline{L}_3 = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{7.16}$$

was introduced. We can write the equations above in short form $(\underline{L}_i)_{jk} = \epsilon_{ijk}$. The general orientation preserving rotation in three dimensions therefore has the form

$$\underline{R}(\boldsymbol{\varphi}) = \exp(\boldsymbol{\varphi} \cdot \underline{\boldsymbol{L}}).$$

Expansion of the exponential function and ordering into even and odd powers of $\boldsymbol{\varphi} \cdot \underline{\boldsymbol{L}}$ yields the representation

$$\underline{R}(\boldsymbol{\varphi}) = \hat{\boldsymbol{\varphi}} \otimes \hat{\boldsymbol{\varphi}}^T + \left(\underline{1} - \hat{\boldsymbol{\varphi}} \otimes \hat{\boldsymbol{\varphi}}^T\right) \cos(\varphi) + \hat{\boldsymbol{\varphi}} \cdot \underline{\boldsymbol{L}} \sin(\varphi). \tag{7.17}$$

[1] See Appendix F for the calculation of the logarithm of an invertible matrix.

[2] Inversion of three axes is equivalent to inversion of one axis combined with a rotation.

Application of the matrix $\hat{\boldsymbol{\varphi}} \cdot \underline{\boldsymbol{L}}$ on a vector $\boldsymbol{r}$ generates a vector product,

$$(\hat{\boldsymbol{\varphi}} \cdot \underline{\boldsymbol{L}}) \cdot \boldsymbol{r} = -\hat{\boldsymbol{\varphi}} \times \boldsymbol{r},$$

i.e. for every vector $\boldsymbol{r}$, the first term in (7.17) preserves the part $\boldsymbol{r}_\parallel = \hat{\boldsymbol{\varphi}} \otimes \hat{\boldsymbol{\varphi}}^T \cdot \boldsymbol{r}$ of the vector which is parallel to the vector $\boldsymbol{\varphi}$, the second term multiplies the orthogonal part $\boldsymbol{r}_\perp = \boldsymbol{r} - \boldsymbol{r}_\parallel$ by the factor $\cos(\varphi)$, and the third part takes the orthogonal part, rotates it by $\pi/2$ and multiplies it by the factor $\sin(\varphi)$,

$$\underline{R}(\boldsymbol{\varphi}) \cdot \boldsymbol{r} = \boldsymbol{r}_\parallel + \boldsymbol{r}_\perp \cos(\varphi) - \hat{\boldsymbol{\varphi}} \times \boldsymbol{r} \sin(\varphi).$$

This also implies that the direction $\hat{\boldsymbol{\varphi}}$ of the vector $\boldsymbol{\varphi}$ is the direction of the axis of rotation.
Exponentiation of the linear combinations $\boldsymbol{\varphi} \cdot \underline{\boldsymbol{L}}$ of the matrices (7.16) thus generates rotations in three dimensions, and therefore these matrices are also denoted as three-dimensional representations of *generators* of the rotation group. They satisfy the commutation relations

$$[\underline{L}_i, \underline{L}_j] = -\epsilon_{ijk} \underline{L}_k. \tag{7.18}$$

We will also use the hermitian matrices

$$\underline{M}_i = -\mathrm{i}\hbar \underline{L}_i, \quad [\underline{M}_i, \underline{M}_j] = \mathrm{i}\hbar \epsilon_{ijk} \underline{M}_k, \quad [\underline{M}_i, \underline{\boldsymbol{M}}^2] = 0. \tag{7.19}$$

It is no coincidence that the angular momentum operators

$$M_i = \epsilon_{ijk} \mathrm{x}_j \mathrm{p}_k$$

satisfy the same commutation relations. We will see that angular momentum operators also generate rotations, and a set of operators M_i generates rotations if and only if the operators satisfy the commutation relations (7.19). It is a consequence of the general Baker-Campbell-Hausdorff formula in Appendix E that the combination of any two rotations to a new rotation is completely determined by the commutation relations (7.19) of the generators of rotations.

7.5 Matrix representations of the rotation group

We wish to classify all possible representations of the commutation relations (7.19) in vector spaces. To accomplish this, it is convenient to change the basis from $M_x \equiv M_1$ and $M_y \equiv M_2$ to

$$M_\pm = M_1 \pm \mathrm{i} M_2, \quad M_z \equiv M_3.$$

The product $\boldsymbol{M}^2 \equiv M_i M_i$ is then

$$\boldsymbol{M}^2 = \frac{1}{2}(M_+ M_- + M_- M_+) + {M_z}^2 = M_- M_+ + {M_z}^2 + \hbar M_z,$$

and we have the commutation relations in the new basis,

$$[M_z, M_\pm] = \pm\hbar M_\pm, \quad [M_+, M_-] = 2\hbar M_z.$$

Hermiticity[3] implies that we can use a basis where M_z is diagonal with real eigenvalues,

$$M_z|m\rangle = \hbar m|m\rangle, \quad m \in \mathbb{R}.$$

The commutation relations then imply

$$M_\pm|m\rangle = \hbar C_\pm(m)|m \pm 1\rangle,$$

$$C_+(m-1)C_-(m) = 2\hbar m + C_-(m+1)C_+(m), \tag{7.20}$$

and ${M_+}^+ = M_-$ implies

$$C_-(m) = \langle m-1|M_-|m\rangle = (\langle m|{M_+}^+|m-1\rangle)^+ = C_+(m-1)^+.$$

Substitution in equation (7.20) yields

$$|C_+(m)|^2 = |C_+(m-1)|^2 - 2\hbar^2 m.$$

Since the left hand side cannot become negative, there must exist some maximal value ℓ for m such that $C_+(\ell) = 0$, $M_+|\ell\rangle = 0$, and we have

$$|C_+(\ell-1)|^2 = 2\hbar^2\ell, \quad |C_+(\ell-2)|^2 = 2\hbar^2(2\ell-1),$$

and after $n-1$ steps

$$|C_+(\ell-n)|^2 = |C_-(\ell-n+1)|^2 = \hbar^2[2n\ell - n(n-1)]. \tag{7.21}$$

Again, the left hand side cannot become negative, and therefore the expression on the right hand side must terminate for some value N of n, $C_-(\ell-N+1) = 0$, $M_-|\ell-N+1\rangle = 0$. This implies existence of an integer N such that $2\ell = N-1$ and

$$C_+(\ell-N) = C_+(-(N+1)/2) = C_-((1-N)/2) = C_-(-\ell) = 0, \tag{7.22}$$

where an irrelevant possible phase factor was excluded. Therefore we have boundaries

$$-\ell = \frac{1-N}{2} \le m \le \frac{N-1}{2} = \ell \tag{7.23}$$

and $N = 2\ell + 1$ possible values for m both for integer ℓ and half-integer ℓ.

[3]We could do the following calculations in slightly more general form without using hermiticity, and then find hermiticity of the finite-dimensional representations along the way.

Equation (7.21) yields with

$$n = \frac{N-1}{2} - m$$

the equation

$$\begin{aligned} n(N-n) &= \frac{N^2}{4} - \left(m + \frac{1}{2}\right)^2 = \frac{N^2-1}{4} - m(m+1) \\ &= \ell(\ell+1) - m(m+1), \end{aligned}$$

and therefore

$$C_+(m)^2 = \hbar^2 \left(\frac{N^2-1}{4} - m(m+1)\right) = \hbar^2 \left[\ell(\ell+1) - m(m+1)\right],$$

$$C_-(m)^2 = C_+(m-1)^2 = \hbar^2 \left[\ell(\ell+1) - m(m-1)\right].$$

We have found all the hermitian matrix representations of the commutation relations (7.19). The magnetic quantum number m can take values $-\ell \le m \le \ell$, the number of dimensions is $N = 2\ell + 1 \in \mathbb{N}$, and the actions of the angular momentum operators are

$$M_z|\ell, m\rangle = \hbar m|\ell, m\rangle, \ 2\ell \in \mathbb{N}_0, \ m \in \{-\ell, -\ell+1, \ldots, \ell-1, \ell\}, \tag{7.24}$$

$$M_+|\ell, m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m+1)}|\ell, m+1\rangle \tag{7.25}$$

$$M_-|\ell, m\rangle = \hbar\sqrt{\ell(\ell+1) - m(m-1)}|\ell, m-1\rangle \tag{7.26}$$

$$\begin{aligned} M_x|\ell, m\rangle = {} & \frac{\hbar}{2}\sqrt{\ell(\ell+1) - m(m+1)}|\ell, m+1\rangle \\ & + \frac{\hbar}{2}\sqrt{\ell(\ell+1) - m(m-1)}|\ell, m-1\rangle, \end{aligned} \tag{7.27}$$

$$\begin{aligned} M_y|\ell, m\rangle = {} & \frac{\hbar}{2\mathrm{i}}\sqrt{\ell(\ell+1) - m(m+1)}|\ell, m+1\rangle \\ & - \frac{\hbar}{2\mathrm{i}}\sqrt{\ell(\ell+1) - m(m-1)}|\ell, m-1\rangle, \end{aligned} \tag{7.28}$$

$$\boldsymbol{M}^2|\ell, m\rangle = \left(C_+(\ell, m)^2 + \hbar^2 m(m+1)\right)|\ell, m\rangle = \hbar^2\ell(\ell+1)|\ell, m\rangle. \tag{7.29}$$

7.6 Construction of the spherical harmonic functions

We now want to construct the $\boldsymbol{r}$ representations of the angular momentum eigenstates $|\ell, m\rangle$, i.e. we wish to construct the solutions $\langle\vartheta, \varphi|\ell, m\rangle \equiv Y_{\ell,m}(\vartheta, \varphi)$ of the differential equations

$$\begin{aligned} \langle\vartheta, \varphi|\boldsymbol{M}^2|\ell, m\rangle &\equiv -\hbar^2 \left(\frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right) Y_{\ell,m}(\vartheta, \varphi) \\ &= \hbar^2\ell(\ell+1)Y_{\ell,m}(\vartheta, \varphi) \end{aligned}$$

and

$$\langle\vartheta,\varphi|M_z|\ell,m\rangle \equiv \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\varphi}Y_{\ell,m}(\vartheta,\varphi) = \hbar m Y_{\ell,m}(\vartheta,\varphi).$$

Here we used that the angular momentum operators act in $\boldsymbol{r}$ space as differential operators with respect to ϑ and φ, and therefore do not determine the radial dependence of wave functions. The radial part can therefore be left out in their representation[4],

$$\begin{aligned}
\boldsymbol{M}^2 &= -\hbar^2\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta\,|\vartheta,\varphi\rangle\left(\frac{\partial^2}{\partial\vartheta^2}+\cot\vartheta\frac{\partial}{\partial\vartheta}+\frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)\langle\vartheta,\varphi|,\\
M_z &= \frac{\hbar}{\mathrm{i}}\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta\,|\vartheta,\varphi\rangle\frac{\partial}{\partial\varphi}\langle\vartheta,\varphi|,\\
M_+ &= \hbar\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta\,|\vartheta,\varphi\rangle\exp(\mathrm{i}\varphi)\left(\mathrm{i}\cot\vartheta\frac{\partial}{\partial\varphi}+\frac{\partial}{\partial\vartheta}\right)\langle\vartheta,\varphi|,\\
M_- &= \hbar\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta\,|\vartheta,\varphi\rangle\exp(-\mathrm{i}\varphi)\left(\mathrm{i}\cot\vartheta\frac{\partial}{\partial\varphi}-\frac{\partial}{\partial\vartheta}\right)\langle\vartheta,\varphi|.
\end{aligned}$$

The equation

$$\langle\vartheta,\varphi|M_z|\ell,\ell\rangle = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\varphi}\langle\vartheta,\varphi|\ell,\ell\rangle = \hbar\ell\langle\vartheta,\varphi|\ell,\ell\rangle \tag{7.30}$$

implies

$$\langle\vartheta,\varphi|\ell,\ell\rangle = Y_{\ell,\ell}(\vartheta,\varphi) = f_\ell(\vartheta)\exp(\mathrm{i}\ell\varphi).$$

Single valuedness of the eigenstates implies $\ell\in\mathbb{N}_0$.
The equation

$$\langle\vartheta,\varphi|M_+|\ell,\ell\rangle = \hbar\exp(\mathrm{i}\varphi)\left(\frac{\partial}{\partial\vartheta}+\mathrm{i}\cot\vartheta\frac{\partial}{\partial\varphi}\right)\langle\vartheta,\varphi|\ell,\ell\rangle = 0 \tag{7.31}$$

implies

$$\left(\frac{\partial}{\partial\vartheta}-\ell\cot\vartheta\right)f_\ell(\vartheta) = 0,$$

with the solution $f_\ell(\vartheta) = N_\ell^{-1/2}\sin^\ell\vartheta$. The normalization constants are chosen to ensure

$$\int_0^{\pi}d\vartheta\,f_\ell^2(\vartheta)\sin\vartheta = 1.$$

They can be calculated recursively if we note that

$$N_0 = \int_0^{\pi}d\vartheta\,\sin\vartheta = 2$$

[4]Stated differently, we leave out a factor $1 = \int_0^\infty dr r^2|r\rangle\langle r|$.

and

$$\begin{aligned} N_{\ell\geq 1} &= \int_0^\pi d\vartheta\, \sin^{2\ell+1}\vartheta = \int_{-1}^1 d\xi\, (1-\xi^2)^\ell \\ &= \xi(1-\xi^2)^\ell\Big|_{-1}^1 + \int_{-1}^1 d\xi\, 2\ell\xi^2(1-\xi^2)^{\ell-1} \\ &= -2\ell N_\ell + 2\ell N_{\ell-1}. \end{aligned}$$

This yields

$$\begin{aligned} N_\ell &= \frac{2\ell}{2\ell+1}N_{\ell-1} = \frac{2^2\ell(\ell-1)}{(2\ell+1)(2\ell-1)}N_{\ell-2} = \ldots = \frac{2^\ell \ell!}{(2\ell+1)!!}2 \\ &= 2\frac{2^{2\ell}(\ell!)^2}{(2\ell+1)!}, \end{aligned}$$

and therefore

$$\langle\vartheta,\varphi|\ell,\ell\rangle = Y_{\ell,\ell}(\vartheta,\varphi) = \frac{(-)^\ell}{2^{\ell+1}\ell!}\sqrt{\frac{(2\ell+1)!}{\pi}}\exp(\mathrm{i}\ell\varphi)\sin^\ell\vartheta. \tag{7.32}$$

We can get the other eigenfunctions from $\langle\vartheta,\varphi|\ell,\ell\rangle$ through repeated applications of the lowering operator M_-,

$$\begin{aligned} Y_{\ell,m}(\vartheta,\varphi) &= \langle\vartheta,\varphi|\ell,m\rangle = \frac{\langle\vartheta,\varphi|M_-|\ell,m+1\rangle}{\hbar\sqrt{(\ell+m+1)(\ell-m)}} \\ &= \frac{\langle\vartheta,\varphi|(M_-)^2|\ell,m+2\rangle}{\hbar^2\sqrt{(\ell+m+1)(\ell+m+2)(\ell-m)(\ell-m-1)}} = \ldots \\ &= \frac{\langle\vartheta,\varphi|(M_-)^{\ell-m}|\ell,\ell\rangle}{\hbar^{\ell-m}}\,[(\ell+m+1)(\ell+m+2)\times\ldots\times 2\ell \\ &\quad \times(\ell-m)(\ell-m-1)\times\ldots\times 1]^{-1/2} \\ &= \frac{1}{\hbar^{\ell-m}}\sqrt{\frac{(\ell+m)!}{(2\ell)!(\ell-m)!}}\langle\vartheta,\varphi|(M_-)^{\ell-m}|\ell,\ell\rangle \\ &= \sqrt{\frac{(\ell+m)!}{(2\ell)!\cdot(\ell-m)!}} \\ &\quad \times\left[\exp(-\mathrm{i}\varphi)\left(\mathrm{i}\cot\vartheta\frac{\partial}{\partial\varphi} - \frac{\partial}{\partial\vartheta}\right)\right]^{\ell-m} Y_{\ell,\ell}(\vartheta,\varphi). \end{aligned} \tag{7.33}$$

If we substitute $Y_{\ell,\ell}(\vartheta,\varphi)$ from (7.32) into (7.33), we find

$$\begin{aligned}
Y_{\ell,m}(\vartheta,\varphi) &= \frac{(-)^m}{2^{\ell+1}\ell!}\sqrt{\frac{(2\ell+1)\cdot(\ell+m)!}{\pi\cdot(\ell-m)!}}\exp(\mathrm{i}m\varphi) \\
&\quad\times\left[\prod_{n=m+1}^{\ell}\left(n\cot\vartheta+\frac{d}{d\vartheta}\right)\right]\sin^{\ell}\vartheta \\
&= \frac{(-)^m}{2^{\ell+1}\ell!}\sqrt{\frac{(2\ell+1)\cdot(\ell+m)!}{\pi\cdot(\ell-m)!}}\exp(\mathrm{i}m\varphi) \\
&\quad\times\left[\prod_{n=m+1}^{\ell}\left(\sin^{-n}\vartheta\frac{d}{d\vartheta}\sin^{n}\vartheta\right)\right]\sin^{\ell}\vartheta \\
&= \frac{(-)^{\ell}}{2^{\ell+1}\ell!}\sqrt{\frac{(2\ell+1)\cdot(\ell+m)!}{\pi\cdot(\ell-m)!}}\exp(\mathrm{i}m\varphi) \\
&\quad\times\sin^{-m}\vartheta\frac{d^{\ell-m}}{d(\cos\vartheta)^{\ell-m}}\sin^{2\ell}\vartheta. \qquad (7.34)
\end{aligned}$$

Equations (7.33) or (7.34) provide a solution to the problem to construct the spherical harmonic functions. However, it is very common to make the connection to orthogonal polynomials in the interval $[-1,1]$. If we use the following equation for the associated Legendre polynomials,

$$P_{\ell}^{m}(x) = (-)^m\frac{(\ell+m)!}{2^{\ell}\ell!\cdot(\ell-m)!}\left(1-x^2\right)^{-m/2}\frac{d^{\ell-m}}{dx^{\ell-m}}\left(x^2-1\right)^{\ell},$$

we can also write

$$Y_{\ell,m}(\vartheta,\varphi) = (-)^m\sqrt{\frac{(2\ell+1)\cdot(\ell-m)!}{4\pi\cdot(\ell+m)!}}\exp(\mathrm{i}m\varphi)P_{\ell}^{m}(\cos\vartheta). \qquad (7.35)$$

The identity

$$\begin{aligned}
&\left(x^2-1\right)^{m/2}\sqrt{\frac{(\ell-m)!}{(\ell+m)!}}\frac{d^{\ell+m}}{dx^{\ell+m}}\left(x^2-1\right)^{\ell} \\
&= \left(x^2-1\right)^{-m/2}\sqrt{\frac{(\ell+m)!}{(\ell-m)!}}\frac{d^{\ell-m}}{dx^{\ell-m}}\left(x^2-1\right)^{\ell}
\end{aligned}$$

implies

$$Y_{\ell,-m}(\vartheta,\varphi) = (-)^m Y_{\ell,m}^{+}(\vartheta,\varphi).$$

The spherical harmonic functions provide an orthonormal basis on the sphere. The completeness relations are

$$\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta\,Y_{\ell,m}(\vartheta,\varphi)Y_{\ell',m'}^{+}(\vartheta,\varphi) = \delta_{\ell,\ell'}\delta_{m,m'} \qquad (7.36)$$

and

$$\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} Y_{\ell,m}(\vartheta,\varphi)Y^{+}_{\ell,m}(\vartheta',\varphi') = \delta(\hat{\boldsymbol{r}}-\hat{\boldsymbol{r}}') = \delta(\cos\vartheta-\cos\vartheta')\delta(\varphi-\varphi'). \tag{7.37}$$

The lowest order spherical harmonics are

$$Y_{0,0}(\vartheta,\varphi) = \frac{1}{\sqrt{4\pi}}, \quad Y_{1,0}(\vartheta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\vartheta,$$

$$Y_{1,1}(\vartheta,\varphi) = -\sqrt{\frac{3}{8\pi}}\exp(\mathrm{i}\varphi)\sin\vartheta, \quad Y_{1,-1}(\vartheta,\varphi) = \sqrt{\frac{3}{8\pi}}\exp(-\mathrm{i}\varphi)\sin\vartheta.$$

7.7 Basic features of motion in central potentials

Separation of the wave function in equation (7.11)

$$\psi(\boldsymbol{r}) = \psi(r)Y_{\ell,m}(\vartheta,\varphi) \tag{7.38}$$

and use of

$$\boldsymbol{M}^2|\ell,m\rangle = \hbar^2\ell(\ell+1)|\ell,m\rangle$$

yields the radial Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r\psi(r) + \left(\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)\right)\psi(r) = E\psi(r). \tag{7.39}$$

The effective potential for the radial part of the relative motion of the two particles is therefore

$$V_{\mathrm{eff}}(r) = V(r) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2},$$

with a "centrifugal barrier" term $\boldsymbol{M}^2/(2\mu r^2)$ just like in classical mechanics. The reason for this term is essentially the same consistency requirement as in classical mechanics. Classically, two particles with non-vanishing relative angular momentum $\boldsymbol{M}$ can never be in the same location, and the centrifugal barrier term simply reflects this property. Quantum mechanically, non-vanishing relative angular momentum $\boldsymbol{M}$ implies that the particular value $\psi(r=0)$ of the radial wave function must be suppressed, and it must be more strongly suppressed for larger $\boldsymbol{M}^2$.

Equation (7.39) is usually solved by the Sommerfeld method. In the first step one studies the asymptotic equations for small r and for large r, and keeps

only the normalizable solutions or those solutions which approximate Fourier monomials in the asymptotic regions. In the next step one makes an *ansatz* for the full solution by multiplying the asymptotic solutions with a polynomial. Before we apply this method to the hydrogen atom, we will do something that one might find odd at first sight. The simplest case of a radially symmetric potential is $V = 0$, i.e. free motion. It is of interest for scattering theory to discuss free motion with defined angular momentum, when the wave function for a free particle has the form (7.38).

7.8 Free spherical waves: the free particle with sharp M_z, M^2

The radial Schrödinger equation for a free particle with fixed angular momentum M_z, $\boldsymbol{M}^2$ and energy $E = \hbar^2 k^2/2\mu$ is

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r\psi(r) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\psi(r) = E\psi(r),$$

or

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right) r\psi(r) = 0. \tag{7.40}$$

The regular solution for $\ell = 0$ is

$$\psi_{k,0}(r) = \sqrt{\frac{2}{\pi}}\frac{\sin(kr)}{kr},$$

where the pre-factor was determined from the normalization condition

$$\int_0^\infty dr\, r^2 \psi_{k,0}(r)\psi_{k',0}(r) = \frac{1}{kk'}\delta(k-k').$$

For the study of solutions $\psi_{k,\ell}(r)$ for higher ℓ, we observe that solutions of equation (7.40) for $kr \ll \sqrt{\ell(\ell+1)}$ are $\psi(r) \propto r^\ell$ or $\psi(r) \propto r^{-\ell-1}$. We will only study solutions which are regular for $r = 0$, i.e. for $kr \ll \sqrt{\ell(\ell+1)}$ our solutions must approximate r^ℓ. Therefore we substitute $\psi_{k,\ell}(r) = r^\ell f_{k,\ell}(r)$ into equation (7.40),

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}(\ell+1)\frac{d}{dr} + k^2\right) f_{k,\ell}(r) = 0.$$

It is useful to write this as

$$\left(r^2\frac{d}{dr}\frac{1}{r^2}\frac{d}{dr} + \frac{2}{r}(\ell+2)\frac{d}{dr} + k^2\right) f_{k,\ell}(r) = 0$$

because the resulting equation after application of $(1/r)d/dr$

$$\left(\frac{1}{r}\frac{d}{dr}r^2\frac{d}{dr}\frac{1}{r}+\frac{2}{r}(\ell+2)\frac{d}{dr}+k^2\right)\frac{1}{r}\frac{d}{dr}f_{k,\ell}(r)$$

$$=\left(\frac{1}{r}\frac{d}{dr}r\frac{d}{dr}-\frac{1}{r}\frac{d}{dr}+\frac{2}{r}(\ell+2)\frac{d}{dr}+k^2\right)\frac{1}{r}\frac{d}{dr}f_{k,\ell}(r)$$

$$=\left(\frac{d^2}{dr^2}+\frac{2}{r}(\ell+2)\frac{d}{dr}+k^2\right)\frac{1}{r}\frac{d}{dr}f_{k,\ell}(r)=0, \tag{7.41}$$

yields

$$f_{k,\ell+1}(r)\propto\frac{1}{r}\frac{d}{dr}f_{k,\ell}(r),\quad \psi_{k,\ell+1}(r)\propto r^\ell\frac{d}{dr}r^{-\ell}\psi_{k,\ell}(r). \tag{7.42}$$

This implies

$$f_{k,\ell}(r)\propto\left(\frac{1}{r}\frac{d}{dr}\right)^\ell f_{k,0}(r)=\sqrt{\frac{2}{\pi}}\left(\frac{1}{r}\frac{d}{dr}\right)^\ell\frac{\sin(kr)}{r},$$

$$\psi_{k,\ell}(r)\propto\sqrt{\frac{2}{\pi}}r^\ell\left(\frac{1}{r}\frac{d}{dr}\right)^\ell\frac{\sin(kr)}{r}=(-)^\ell k^\ell\sqrt{\frac{2}{\pi}}j_\ell(kr).$$

The spherical Bessel functions

$$j_\ell(x)=(-x)^\ell\left(\frac{1}{x}\frac{d}{dx}\right)^\ell\frac{\sin x}{x}=\sqrt{\frac{\pi}{2x}}J_{\ell+\frac{1}{2}}(x)$$

have the asymptotic expansion

$$j_\ell(x)\Big|_{x\gg1}\approx\frac{1}{x}\sin\left(x-\frac{\pi\ell}{2}\right).$$

Therefore the properly normalized radial eigenfunctions are

$$\psi_{k,\ell}(r)=\sqrt{\frac{2}{\pi}}\mathrm{i}^\ell j_\ell(kr)=\sqrt{\frac{2}{\pi}}\left(\frac{r}{\mathrm{i}k}\right)^\ell\left(\frac{1}{r}\frac{d}{dr}\right)^\ell\frac{\sin(kr)}{kr}, \tag{7.43}$$

and the free spherical waves with sharp angular momenta $\boldsymbol{M}^2$, M_z are

$$\langle\boldsymbol{r}|k,\ell,m\rangle=\sqrt{\frac{2}{\pi}}\mathrm{i}^\ell j_\ell(kr)Y_{\ell,m}(\vartheta,\varphi)=\frac{\mathrm{i}^\ell}{\sqrt{kr}}J_{\ell+\frac{1}{2}}(kr)Y_{\ell,m}(\vartheta,\varphi). \tag{7.44}$$

Our conventions for the phase and the normalization of the radial wave function are motivated by the expansion of plane waves in terms of spherical harmonics. If we define

$$\langle\boldsymbol{k}|k',\ell,m\rangle=\frac{1}{kk'}\delta(k-k')Y_{\ell,m}(\hat{\boldsymbol{k}}),$$

we automatically get the expansion of plane waves in terms of spherical harmonics,

$$\langle \boldsymbol{r}|\boldsymbol{k}\rangle = \frac{1}{\sqrt{2\pi}^3}\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) = \sqrt{\frac{2}{\pi}}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\mathrm{i}^{\ell}j_{\ell}(kr)Y_{\ell,m}(\hat{\boldsymbol{r}})Y^{+}_{\ell,m}(\hat{\boldsymbol{k}})$$
$$= \frac{1}{\sqrt{kr}}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\mathrm{i}^{\ell}J_{\ell+\frac{1}{2}}(kr)Y_{\ell,m}(\hat{\boldsymbol{r}})Y^{+}_{\ell,m}(\hat{\boldsymbol{k}}). \tag{7.45}$$

This expansion is also particularly useful for $\exp(\mathrm{i}kz)$. We have $P^m_{\ell}(1) = \delta_{m,0}$ and therefore $Y_{\ell,m}(\boldsymbol{e}_z) = Y_{\ell,m}(\vartheta = 0) = \sqrt{(2\ell+1)/4\pi}$. This yields

$$\exp(\mathrm{i}kz) = \sum_{\ell=0}^{\infty}(2\ell+1)\mathrm{i}^{\ell}j_{\ell}(kr)P_{\ell}(\cos\vartheta). \tag{7.46}$$

The radial wave functions (7.43) of the free spherical waves (7.44) satisfy completeness relations on the half-line

$$\int_0^{\infty} dr\, r^2\,\psi_{k,\ell}(r)\psi_{k',\ell}(r) = \frac{1}{k^2}\delta(k-k'),$$

$$\int_0^{\infty} dk\, k^2\,\psi_{k,\ell}(r)\psi_{k,\ell}(r') = \frac{1}{r^2}\delta(r-r'). \tag{7.47}$$

If our discussion above does not refer to motion of a single particle with mass μ, but to relative motion of two non-interacting particles at locations

$$\boldsymbol{x}_1 = \boldsymbol{R} + \frac{m_2}{m_1+m_2}\boldsymbol{r}, \quad \boldsymbol{x}_2 = \boldsymbol{R} - \frac{m_1}{m_1+m_2}\boldsymbol{r}$$

we can write a full two-particle wave function with sharp angular momentum quantum numbers for the relative motion as

$$\langle \boldsymbol{R},\boldsymbol{r}|\boldsymbol{K},k,\ell,m\rangle = \frac{\mathrm{i}^{\ell}}{2\pi^2}\exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R})j_{\ell}(kr)Y_{\ell,m}(\hat{\boldsymbol{r}}),$$

or we could also require sharp angular momentum quantum numbers L, M for the center or mass motion[5],

$$\langle \boldsymbol{R},\boldsymbol{r}|K,L,M,k,\ell,m\rangle = \frac{2}{\pi}\mathrm{i}^{L+\ell}j_L(KR)j_{\ell}(kr)Y_{L,M}(\hat{\boldsymbol{R}})Y_{\ell,m}(\hat{\boldsymbol{r}}).$$

[5] ... or we could use total angular momentum, i.e. quantum numbers $K,k,j \in \{|L-\ell|,\ldots,L+\ell\}, m_j = M+m, L, \ell$.

7.9 Bound energy eigenstates of the hydrogen atom

The solution for the hydrogen atom was reported by Schrödinger in 1926 in the same paper where he introduced the time-independent Schrödinger equation[6]. We recall that separation of the wave function in equation (7.11)

$$\psi(\boldsymbol{r}) = \psi(r)Y_{\ell,m}(\vartheta,\varphi) \tag{7.48}$$

and use of $\boldsymbol{M}^2|\ell,m\rangle = \hbar^2\ell(\ell+1)|\ell,m\rangle$ yields the radial Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r\psi(r) + \left(\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} - \frac{e^2}{4\pi\epsilon_0 r}\right)\psi(r) = E\psi(r), \tag{7.49}$$

where the attractive Coulomb potential between charges e and $-e$ has been inserted. This yields asymptotic equations for small r,

$$-r^2\frac{d^2}{dr^2}r\psi(r) + \ell(\ell+1)r\psi(r) = 0, \tag{7.50}$$

and for large r,

$$-\frac{d^2}{dr^2}r\psi(r) = \frac{2\mu E}{\hbar^2}r\psi(r). \tag{7.51}$$

The Euler type differential equation (7.50) has basic solutions $r\psi(r) = Ar^{\ell+1} + Br^{-\ell}$, but with $\ell \geq 0$ only the first solution $r\psi(r) \propto r^{\ell+1}$ will yield a finite probability density $|\psi(\boldsymbol{r})|^2$ near the origin.
The normalizable solution of (7.51) for $E < 0$ is

$$r\psi(r) \propto \exp\left(-\sqrt{-2\mu E}r/\hbar\right). \tag{7.52}$$

We combine the asymptotic solutions with a polynomial $w(r) = \sum_{\nu\geq 0} c_\nu r^\nu$,

$$r\psi(r) = r^{\ell+1}w(r)\exp(-\kappa r), \quad \kappa = \sqrt{-2\mu E}r/\hbar.$$

Substitution in (7.49) yields the condition

$$r\frac{d^2}{dr^2}w(r) + 2(\ell+1-\kappa r)\frac{d}{dr}w(r) + \left(\frac{\mu e^2}{2\pi\epsilon_0\hbar^2} - 2\kappa(\ell+1)\right)w(r) = 0,$$

which in turn yields a recursion relation for the coefficients in the polynomial $w(r)$,

$$c_{\nu+1} = c_\nu\frac{2\kappa(\nu+\ell+1) - \frac{\mu e^2}{2\pi\epsilon_0\hbar^2}}{(\nu+1)(\nu+2\ell+2)}. \tag{7.53}$$

[6] E. Schrödinger, Annalen Phys. 384, 361 (1926).

Normalizability of the solution requires termination of the polynomial $w(r)$ with a maximal power $N \equiv \max(\nu) \geq 0$ of r, i.e. $c_{N+1} = 0$ and therefore

$$\kappa \equiv \frac{\sqrt{-2\mu E}}{\hbar} = \frac{\mu e^2}{4\pi\epsilon_0 \hbar^2 (N + \ell + 1)}. \tag{7.54}$$

This implies energy quantization for the bound states in the form

$$E_n = -\frac{\mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2} \tag{7.55}$$

with the principal quantum number $n \equiv N+\ell+1$. Note that $N \geq 0$ implies the relation $n \geq \ell + 1$ between the principal and the magnetic quantum number. We will also use equation (7.54) in the form $\kappa = (na)^{-1}$ with the Bohr radius

$$a \equiv \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}. \tag{7.56}$$

The recursion relation is then

$$c_{\nu+1} = c_\nu \frac{2}{na} \frac{\nu + \ell + 1 - n}{(\nu + 1)(\nu + 2\ell + 2)}, \quad 0 \leq \nu \leq N \equiv n - \ell - 1. \tag{7.57}$$

This defines all coefficients c_ν in $w(r)$ in terms of the coefficient c_0, which finally must be determined from normalization. The factor $2/na$ in the recursion relation will generate a power $(2/na)^\nu$ in c_ν, such that $w(r)$ will be a polynomial in $2r/na$. The factor $(\nu + 1)^{-1}$ will generate a factor $1/\nu!$ in c_ν, and the factor $(\nu + \alpha)/(\nu + \beta)$ with $\alpha = \ell + 1 - n$, $\beta = 2\ell + 2$ will finally yield a polynomial of the form

$$\begin{aligned} w(r) = c_0 \Bigg[1 + \frac{\alpha}{\beta} \frac{2r}{na} + \frac{1}{2!} \frac{\alpha(\alpha+1)}{\beta(\beta+1)} \left(\frac{2r}{na}\right)^2 \\ + \frac{1}{3!} \frac{\alpha(\alpha+1)(\alpha+2)}{\beta(\beta+1)(\beta+2)} \left(\frac{2r}{na}\right)^3 + \ldots \Bigg] = c_0 \times {}_1F_1(\alpha; \beta; 2r/na). \end{aligned}$$

As indicated in this equation, the series for $c_0 = 1$ defines the confluent hypergeometric function ${}_1F_1(\alpha; \beta; x) \equiv M(\alpha; \beta; x)$ (also known as Kummer's function [1]). For $-\alpha \in \mathbb{N}_0$ and $\beta \in \mathbb{N}$ this function can also be expressed as an associated Laguerre polynomial. The normalized radial wave functions can then be written as

$$\begin{aligned} \psi_{n,\ell}(r) &= \frac{2}{n^2} \sqrt{\frac{(n+\ell)!}{(n-\ell-1)! a^3}} \frac{{}_1F_1(-n+\ell+1; 2\ell+2; 2r/na)}{(2\ell+1)!} \\ &\quad \times \left(\frac{2r}{na}\right)^\ell \exp\left(-\frac{r}{na}\right) \\ &= \frac{2}{n^2} \sqrt{\frac{(n-\ell-1)!}{(n+\ell)! a^3}} \left(\frac{2r}{na}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na}\right) \exp\left(-\frac{r}{na}\right). \end{aligned} \tag{7.58}$$

Substitution of the explicit series representation for $w(r)$ shows that the radial wave functions are products of a polynomial in $2r/na$ of order $n-1$ with $n-\ell$ terms, multiplied with the exponential function $\exp(-r/na)$,

$$\psi_{n,\ell}(r) = \frac{2}{n^2}(-)^\ell \sqrt{\frac{(n+\ell)!(n-\ell-1)!}{a^3}} \exp\Big(-\frac{r}{na}\Big) \times \sum_{k=\ell}^{n-1} \frac{(-2r/na)^k}{(k-\ell)!(n-k-1)!(k+\ell+1)!}. \tag{7.59}$$

The representation (7.58) in terms of the associated Laguerre polynomials differs from older textbook representations by a factor $(n+\ell)!$ due to the modern definition of the normalization of associated Laguerre polynomials,

$$L_n^m(x) = \frac{(-)^m}{(n+m)!}\frac{d^m}{dx^m}\left(\exp(x)\frac{d^{n+m}}{dx^{n+m}}\left[x^{n+m}\exp(-x)\right]\right) = \frac{(m+n)!}{n!\cdot m!}{}_1F_1(-n;m+1;x),$$

which is also used in symbolic calculation programs. The normalization follows from

$$\int_0^\infty dx\, \exp(-x)x^{m+1}[L_n^m(x)]^2 = (2n+m+1)\frac{(n+m)!}{n!}, \tag{7.60}$$

but their standard orthogonality relation is

$$\int_0^\infty dx\, \exp(-x)x^m L_n^m(x)L_{n'}^m(x) = \frac{(n+m)!}{n!}\delta_{n,n'}. \tag{7.61}$$

Since they appear as eigenstates of the hydrogen Hamiltonian, the normalized bound radial wave functions must satisfy the orthogonality relation

$$\int_0^\infty dr\, r^2\, \psi_{n,\ell}(r)\psi_{n',\ell}(r) = \delta_{n,n'}. \tag{7.62}$$

This implies that the associated Laguerre polynomials must also satisfy a peculiar additional orthogonality relation which generalizes (7.60),

$$\int_0^\infty dx\, \exp\left(-\frac{(n+n'+m+1)x}{(2n+m+1)(2n'+m+1)}\right) x^{m+1}L_n^m\left(\frac{x}{2n+m+1}\right) \times L_{n'}^m\left(\frac{x}{2n'+m+1}\right) = (2n+m+1)^{m+3}\frac{(n+m)!}{n!}\delta_{n,n'}. \tag{7.63}$$

Squares $\psi_{n,\ell}^2(r)$ of the radial wave functions are plotted for low lying values of n and ℓ in Figures 7.1-7.6.

For the meaning of the radial wave function, recall that the full three-dimensional wave function is

$$\psi_{n,\ell,m}(\boldsymbol{r}) = \psi_{n,\ell}(r)Y_{\ell,m}(\vartheta,\varphi).$$

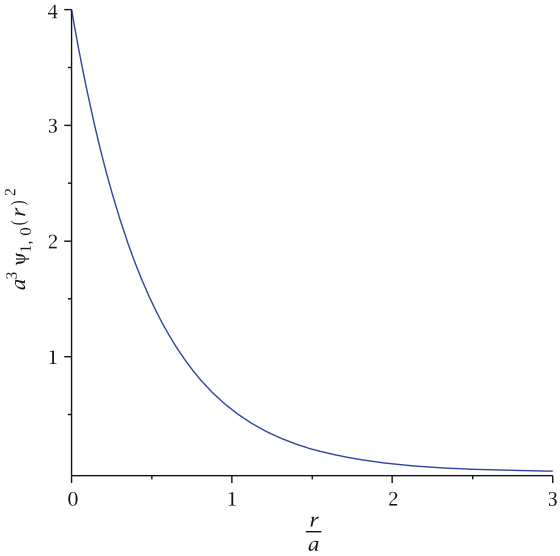


Figure 7.1: The function $a^3\psi_{1,0}^2(r)$.

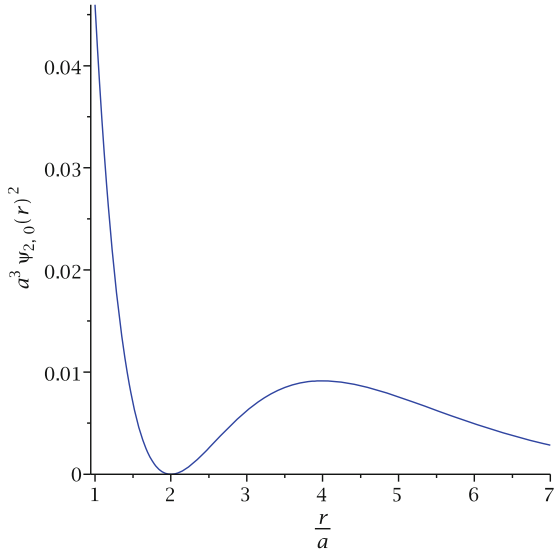


Figure 7.2: The function $a^3\psi_{2,0}^2(r)$ for $r > a$.

This implies that $\psi_{n,\ell}^2(r)$ is a radial profile of the probability density $|\psi_{n,\ell,m}(\boldsymbol{r})|^2$ to find the particle (or rather the quasi-particle which describes relative motion

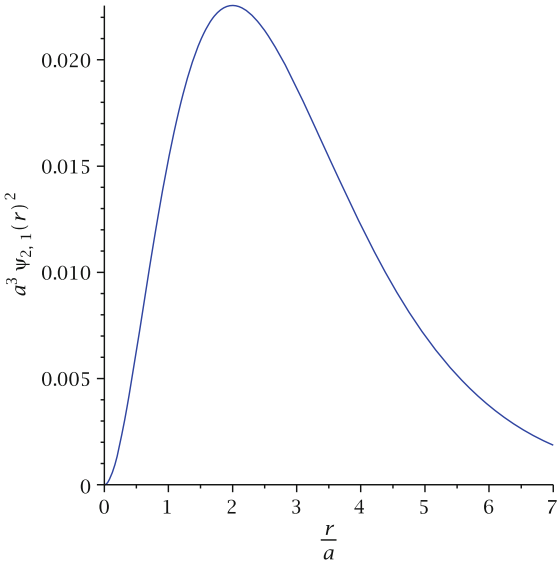


Figure 7.3: The function $a^3\psi^2_{2,1}(r)$.

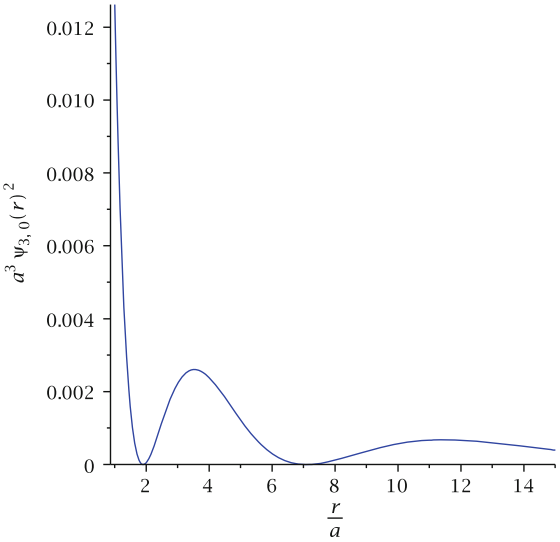


Figure 7.4: The function $a^3\psi^2_{3,0}(r)$ for $r > a$.

in the hydrogen atom) in the location $\boldsymbol{r}$, but note that in each particular direction (ϑ, φ) the radial profile is scaled by the factor $Y^2_{\ell,m}(\vartheta, \varphi)$ to give the

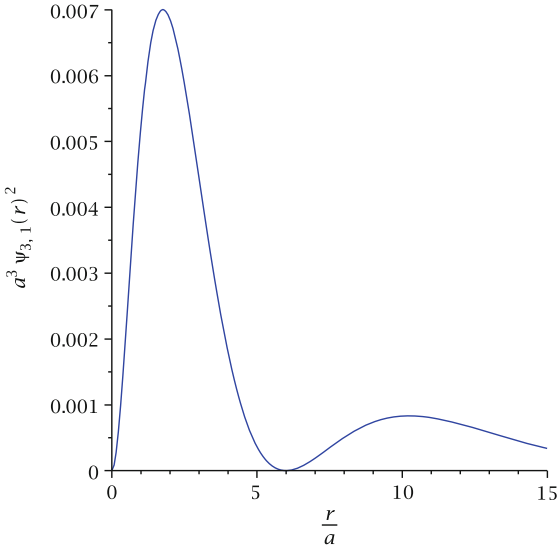


Figure 7.5: The function $a^3\psi^2_{3,1}(r)$.

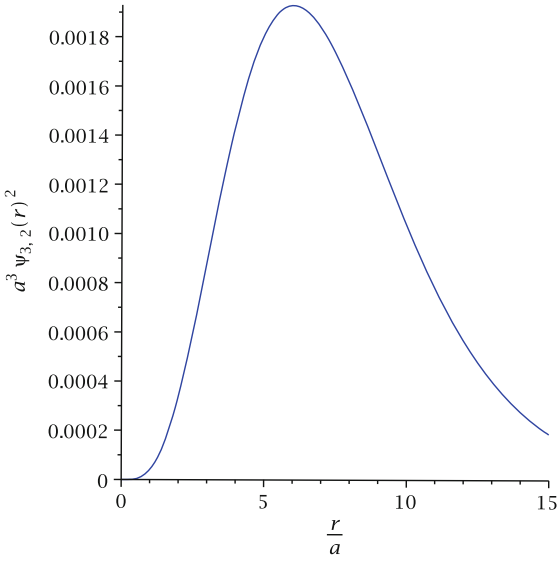


Figure 7.6: The function $a^3\psi^2_{3,2}(r)$.

actual radial profile of the probability density in that direction. Furthermore, note that the probability density for finding the electron-proton pair with

separation between r and $r + dr$ is

$$\int_0^\pi d\vartheta \int_0^{2\pi} d\varphi\, r^2 \sin\vartheta\ |\psi_{n,\ell,m}(\boldsymbol{r})|^2 = r^2 \psi_{n,\ell}^2(r).$$

The function $\psi_{n,\ell}^2(r)$ is proportional to the radial probability density in fixed directions, while $r^2\psi_{n,\ell}^2(r)$ samples the full spherical shell between r and $r+dr$ in all directions, and therefore the latter probability density is scaled by the geometric size factor r^2 for thin spherical shells.
Nowadays radial expectation values

$$\langle r^h \rangle_{n,\ell} = \int_0^\infty dr\, r^{h+2} \psi_{n,\ell}^2(r)$$

are readily calculated with symbolic computation programs. One finds in particular

$$\langle r \rangle_{n,\ell} = \frac{3n^2 - \ell(\ell+1)}{2} a, \quad \langle r^2 \rangle_{n,\ell} = \frac{n^2}{2}[5n^2 + 1 - 3\ell(\ell+1)]a^2.$$

The resulting uncertainty in distance between the proton and the electron

$$(\Delta r)_{n,\ell} = \langle r^2 \rangle_{n,\ell} - \langle r \rangle_{n,\ell}^2 = \frac{a}{2}\sqrt{n^2(n^2+2) - \ell^2(\ell+1)^2}$$

is relatively large for most states in the sense that $(\Delta r/\langle r \rangle)_{n,\ell}$ is not small, except for large n states with large angular momentum. For example, $(\Delta r/\langle r \rangle)_{n,0}$ $= \sqrt{1 + (2/n^2)}/3 > 1/3$ but $(\Delta r/\langle r \rangle)_{n,n-1} = 1/\sqrt{2n+1}$. However, even for large n and ℓ, the particle could still have magnetic quantum number $m = 0$, whence its probability density would be uniformly spread over directions (ϑ, φ). This means that a hydrogen atom with sharp energy generically cannot be considered as consisting of a well localized electron near a well localized proton. This is just another illustration of the fact that simple particle pictures make no sense at the quantum level.
We also note from (7.58) or (7.59) that the bound energy eigenstates $\psi_{n,\ell,m}(\boldsymbol{r})$ $= \psi_{n,\ell}(r) Y_{\ell,m}(\vartheta, \varphi)$ have a typical linear scale

$$na = n\frac{4\pi\epsilon_0 \hbar^2}{\mu Z e^2} \propto n\frac{\mu^{-1}}{Ze^2}. \tag{7.64}$$

Here we have generalized the definition of the Bohr radius a to the case of an electron in the field of a nucleus of charge Ze. Equation (7.64) is another example of the competition between the kinetic term $p^2/2\mu$ driving wave packets apart, and an attractive potential, here $V(r) = -Ze^2/4\pi\epsilon_0 r$, trying to collapse the wave function into a point. Metaphorically speaking, pressure from kinetic terms stabilizes the wave function. For given ratio of force constant Ze^2 and kinetic parameter μ^{-1} the attractive potential cannot compress the wave packet to sizes smaller than a, and therefore there is no way for the system to release any more energy. Superficially, there seems to exist a classical

analog to the quantum mechanical competition between kinetic energy and attractive potentials in the Schrödinger equation. In classical mechanics, competition between centrifugal terms and attractive potentials can yield stable bound systems. However, the classical analogy is incomplete in a crucial point. The centrifugal term for $\ell \neq 0$ is also there in equation (7.49) exactly as in the classical Coulomb or Kepler problems. However, what stabilizes the wave function against core collapse in the crucial lowest energy case with $\ell = 0$ is the radial kinetic term, whereas in the classical case bound Coulomb or Kepler systems with vanishing angular momentum always collapse. To understand the quantum mechanical stabilization of atoms against collapse a little better, let us repeat equation (7.49) for $\ell = 0$ and nuclear charge Ze, and for low values of r, where we can assume $\psi(r) \neq 0$:

$$\frac{\hbar^2}{2\mu}\frac{1}{\psi(r)}\frac{d^2}{dr^2}r\psi(r) = -Er - \frac{Ze^2}{4\pi\epsilon_0}. \tag{7.65}$$

The radial probability amplitude $r\psi(r)$ must satisfy $\psi^{-1}(r)d^2(r\psi(r))/dr^2 < 0$ near the origin, to bend the function around to eventually yield $\lim_{r\to\infty} r\psi(r) = 0$, which is necessary for normalizability of $r^2\psi^2(r)$ on the half-axis $r > 0$. But near $r = 0$, the only term that bends the wave function in the right direction for normalizability is essentially the ratio Ze^2/μ^{-1},

$$\frac{1}{\psi(r)}\frac{d^2}{dr^2}r\psi(r) \simeq -\frac{Ze^2\mu}{2\pi\epsilon_0\hbar^2}.$$

If we want to concentrate more and more of the wave function near the origin $r \simeq 0$, we have to bend it around already very close to $r = 0$ to reach small values $ar^2\psi^2(r) \ll 1$ very early. But the only parameter that bends the wave function near the origin $r \simeq 0$ is the ratio between attractive force constant and kinetic parameter, Ze^2/μ^{-1}. This limits the minimal spatial extension of the wave function and therefore prevents the classically inevitable core collapse in the bound Coulomb system with $\boldsymbol{L} = \boldsymbol{0}$. In a nutshell, there is only so much squeezing of the wave function that Ze^2/μ^{-1} can do. See also Problem 13 for squeezing or stretching of a hydrogen atom near its ground state.
The radial probability amplitude $r\psi_{1,0}(r)$ for the ground state is plotted in Figure 7.7.

7.10 Spherical Coulomb waves

Now we assume $E > 0$. Recall that the asymptotic solutions for $r\psi(r)$ for $r \to 0$ were of the form $Ar^{\ell+1} + Br^{-\ell}$. Let us initially focus on the solutions which remain regular in the origin.
The symptotic behavior for large r *seems* to correspond to outgoing and incoming radial waves

$$r\psi_{\pm}(r) \to A_{\pm}\exp(\pm \mathrm{i}kr), \quad k = \sqrt{2\mu E}/\hbar.$$

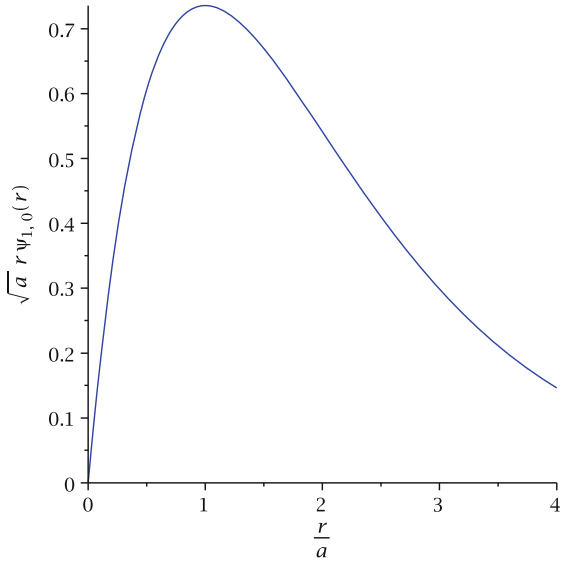


Figure 7.7: The function $\sqrt{a}r\psi_{1,0}(r)$.

Therefore we try an *ansatz*

$$r\psi_{\pm}(r) = w_{\pm}(r)r^{\ell+1}\exp(\pm \mathrm{i}kr), \quad w_{\pm}(r) = \sum_{\nu\geq 0} c_{\pm,\nu} r^{\nu}.$$

Instead of the recursion relation (7.53) we now find

$$c_{\pm,\nu+1} = -c_{\pm,\nu}\frac{2}{\nu+1}\frac{\frac{1}{a} \pm \mathrm{i}k(\nu+\ell+1)}{\nu+2\ell+2} \tag{7.66}$$

and therefore

$$\begin{aligned} w_{\pm}(r) \propto\ & 1 \mp \frac{\ell+1\mp\frac{\mathrm{i}}{ka}}{2\ell+2}2\mathrm{i}kr + \frac{\left(\ell+1\mp\frac{\mathrm{i}}{ka}\right)\left(\ell+2\mp\frac{\mathrm{i}}{ka}\right)}{(2\ell+2)(2\ell+3)}\frac{(2\mathrm{i}kr)^2}{2!} \\ & \mp\frac{\left(\ell+1\mp\frac{\mathrm{i}}{ka}\right)\left(\ell+2\mp\frac{\mathrm{i}}{ka}\right)\left(\ell+3\mp\frac{\mathrm{i}}{ka}\right)}{(2\ell+2)(2\ell+3)(2\ell+4)}\frac{(2\mathrm{i}kr)^3}{3!} + \dots \\ =\ & {}_1F_1(\ell+1\mp(\mathrm{i}/ka); 2\ell+2; \mp 2\mathrm{i}kr). \end{aligned}$$

However, the confluent hypergeometric function satisfies Kummer's identity

$${}_1F_1(\alpha;\beta;z) = \exp(z){}_1F_1(\beta-\alpha;\beta;-z),$$

and this implies in particular

$$\exp(\mathrm{i}kr){}_1F_1(\ell+1-(\mathrm{i}/ka); 2\ell+2; -2\mathrm{i}kr)$$

$$= \exp(-\mathrm{i}kr)\,{}_1F_1(\ell+1+(\mathrm{i}/ka);2\ell+2;2\mathrm{i}kr),$$

i.e. there is only one regular solution for given quantum numbers (k,ℓ), and it corresponds neither to an outgoing nor to an incoming spherical wave, but is apparently rather a superposition of incoming and outgoing waves. For applications in scattering theory one often also has to look at solutions which are irregular in the origin,

$$r\psi(r) = r^{-\ell}v_\pm(r)\exp(\pm\mathrm{i}kr), \quad v_\pm(r) = \sum_{\nu\geq 0} d_{\pm,\nu}r^\nu.$$

In this case, the radial Schrödinger equation yields

$$d_{\pm,\nu+1} = \mp d_{\pm,\nu}\frac{2\mathrm{i}k}{\nu+1}\frac{\nu-\ell\mp\frac{\mathrm{i}}{ka}}{\nu-2\ell}. \tag{7.67}$$

This recursion relation follows also directly from (7.66) with the substitution $\ell\to-\ell-1$. The solution is

$$v_\pm(r) \propto {}_1F_1(-\ell\mp(\mathrm{i}/ka);-2\ell;\mp2\mathrm{i}kr),$$

and we have again from Kummer's identity

$$\exp(\mathrm{i}kr)\,{}_1F_1(-\ell-(\mathrm{i}/ka);-2\ell;-2\mathrm{i}kr)$$

$$= \exp(-\mathrm{i}kr)\,{}_1F_1(-\ell+(\mathrm{i}/ka);-2\ell;2\mathrm{i}kr),$$

i.e. there is also only one irregular solution for given quantum numbers (k,ℓ), as expected. Regular and irregular solutions can be combined to form outgoing or incoming spherical waves, see e.g. [1] or [26]. This is relevant when the long range Coulomb potential is combined with a short range scattering potential, because the short range part will modify the short distance properties of the states and both the regular and irregular spherical Coulomb waves are then needed to model the asymptotic behavior of incoming and scattered waves far from the short range scattering potential. This is relevant for scattering in nuclear physics, when short range scattering is effected by nuclear forces.
However, for us the regular solutions are more interesting because together with the bound states $\psi_{n,\ell,m}(\boldsymbol{r}) = \psi_{n,\ell}(r)Y_{\ell,m}(\vartheta,\varphi)$, the regular unbound states $\psi_{k,\ell,m}(\boldsymbol{r}) = \psi_{k,\ell}(r)Y_{\ell,m}(\vartheta,\varphi)$ form a complete set in Hilbert space.
We use the normalization[7]

$$\begin{aligned}\psi_{k,\ell}(r) = {}& \sqrt{\frac{2}{\pi}}\exp\Big(\frac{\pi}{2ak}\Big)\frac{\big|\Gamma\big(\ell+1+\frac{\mathrm{i}}{ka}\big)\big|}{(2\ell+1)!}(2kr)^\ell\exp(-\mathrm{i}kr)\\ &\times{}_1F_1(\ell+1+(\mathrm{i}/ka);2\ell+2;2\mathrm{i}kr).\end{aligned} \tag{7.68}$$

[7] W. Gordon, Annalen Phys. 394, 1031 (1929); M. Stobbe, Annalen Phys. 399, 661 (1930), see also [2]. Gordon and Stobbe normalized in the k scale, i.e. to $\delta(k-k')$ instead of $\delta(k-k')/k^2$.

With this normalization the regular spherical Coulomb waves become the free waves with sharp angular momentum (7.43) in the limit of vanishing Coulomb potential $e^2 \to 0 \;\Rightarrow\; a \to \infty$.

Apart from the normalization, the spherical Coulomb waves $\psi_{k,\ell}(r)$ become the radial bound state wave functions $\psi_{n,\ell}(r)$ through the substitution $\mathrm{i}k \to (na)^{-1}$. This is expected since this substitution takes the positive energy Schrödinger equation into the negative energy Schrödinger equation.

The regular spherical Coulomb waves satisfy the orthogonality properties (cf. (7.62))

$$\int_0^\infty dr\, r^2\, \psi_{k,\ell}(r)\psi_{k',\ell}(r) = \frac{1}{k^2}\delta(k-k'), \qquad \int_0^\infty dr\, r^2\, \psi_{k,\ell}(r)\psi_{n,\ell}(r) = 0,$$

and together with the radial bound state wave functions they satisfy the completeness relation[8]

$$\sum_{n=\ell+1}^{\infty} \psi_{n,\ell}(r)\psi_{n,\ell}(r') + \int_0^\infty dk\, k^2 \psi_{k,\ell}(r)\psi_{k,\ell}(r') = \frac{1}{r^2}\delta(r-r').$$

Together with the completeness relation (7.37) for the spherical harmonics, this implies completeness of the regular hydrogen states,

$$\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\left(\sum_{n=\ell+1}^{\infty}\psi_{n,\ell,m}(\boldsymbol{r})\psi^+_{n,\ell,m}(\boldsymbol{r}') + \int_0^\infty dk\, k^2 \psi_{k,\ell,m}(\boldsymbol{r})\psi^+_{k,\ell,m}(\boldsymbol{r}')\right)$$
$$= \delta(\boldsymbol{r}-\boldsymbol{r}'). \tag{7.69}$$

For calculations of transitions between free and bound states, e.g. for electron-proton recombination cross sections, one needs free eigenstates which are not radially symmetric but approximate plane waves at large separations. To construct such a state from the spherical Coulomb waves, we can use that equation (7.46) tells us the decomposition of the plane wave $\exp(\mathrm{i}kz)$ in terms of the free states of sharp angular momentum (7.43),

$$\exp(\mathrm{i}kz) = \sqrt{\frac{\pi}{2}}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(\cos\vartheta)\psi^{(e^2=0)}_{k,\ell}(r).$$

However, one needs to adjust the phase factors in the sum if one wants to get an asymptotic superposition of plane waves and outgoing spherical waves. The superposition of spherical Coulomb waves[9] (7.68),

$$\langle \boldsymbol{r}|k\rangle_{MG} = \sqrt{\frac{\pi}{2}}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(\cos\vartheta)\frac{\Gamma\left(\ell+1+\frac{\mathrm{i}}{ka}\right)}{\left|\Gamma\left(\ell+1+\frac{\mathrm{i}}{ka}\right)\right|}\psi_{k,\ell}(r), \tag{7.70}$$

will correspond to a free energy eigenstate of hydrogen with energy $\hbar^2k^2/2\mu$ which up to logarithmic corrections approximates a superposition of a plane wave $\exp(\mathrm{i}kz)$ with outgoing radial waves.

[8] See e.g. N. Mukunda, Amer. J. Phys. 46, 910 (1978).

[9] N.F. Mott, Proc. Roy. Soc. London A 118, 542 (1928); W. Gordon, Z. Phys. 48, 180 (1928).

7.11 Problems

7.1 How large is the minimal value of the product $\Delta M_x \Delta M_y$ of uncertainties of angular momentum components in a state $|\ell, m_\ell\rangle$?

7.2 A simple spherical model for a color center or a quantum dot consists of an electron confined to a sphere of radius R. Inside the sphere the electron can move freely because the potential energy vanishes there, $V(r) = 0$ for $r < R$. The wave function in the sphere for given angular momentum quantum numbers will therefore have the form $\psi(\boldsymbol{r}) \propto j_\ell(kr) Y_{\ell,m}(\vartheta, \varphi)$.
Which energy quantization conditions will we get from the condition that the wave function vanishes for $r \geq R$? How large is the radius R if the electron absorbs photons of energy 2.3 eV?
Zeros $x_{n,\ell}$ of spherical Bessel functions, $j_\ell(x_{n,\ell}) = 0$, $n = 1, 2, \ldots$ can be found e.g. in Chapter 10 of [1].
Which relation between R and lattice constant d follows from Mollwo's relation $\nu d^2 = 5.02 \times 10^{-5}\,\mathrm{m^2 Hz}$?
In hindsight, color centers could be considered as the first realization of atomic scale quantum dots.

7.3 Show that the radial density profile $\psi^2_{n,\ell}(r)$ for bound states of hydrogen has maxima at the extrema of the radial wave function $\psi_{n,\ell}(r)$.
Remark: $\psi_{n,\ell}(r)$ and $d\psi_{n,\ell}(r)/dr$ have no common zeros, because this would contradict the radial Schrödinger equation.

7.4 Calculate the radius $r^{(n,n-1)}_{max}$ where the radial wave function $\psi_{n,n-1}(r)$ has a maximum. Compare your result to $\langle r\rangle_{n,n-1} \pm (\Delta r)_{n,n-1}$.

7.5 For $n \geq 2$ calculate the radius $r^{(n,n-2)}_{max}$ where the radial wave function $\psi_{n,n-2}(r)$ has a maximum.

7.6 As a rule of thumb, quantum systems tend to approach classical behavior for large quantum numbers. We have seen that for large quantum number n the radial wave function $\psi_{n,n-1}(r)$ is localized in a spherical shell $\langle r\rangle_{n,n-1} \pm (\Delta r)_{n,n-1}$ which is "thin" in the sense of $(\Delta r/\langle r\rangle)_{n,n-1} = 1/\sqrt{2n+1} \to 0$.
For sharp energy $E_{n,\ell,m}$, could we ever hope to find an approximately localized electron in a hydrogen atom?

7.7 Calculate the radial expectation values $\langle r^{-1}\rangle_{n,\ell}$, $\langle r^{-2}\rangle_{n,\ell}$ and $\langle r^{-3}\rangle_{n,\ell}$. These expectation values are relevant for interaction energies within the atom.

7.8 We have seen how the expectation value $\langle r\rangle$ for the separation between the electron and the proton depends on the quantum numbers n and ℓ. How large are the corresponding expectation values for the distances of the two particles from the center of mass of the hydrogen atom?

7.9 An electric field along the z axis shifts the potential energy of a hydrogen atom by a perturbation $\Delta V \propto z$. For which combinations of quantum numbers are the matrix elements $\langle n_1', n_2', m'|z|n_1, n_2, m\rangle$ different from zero?

7.10 Calculate the probability density to find the momentum $\boldsymbol{p}$ in the relative motion inside a hydrogen atom in its ground state.

7.11 Calculate the probability density to find the momentum $\boldsymbol{p}$ in the relative motion inside a hydrogen atom if the atom is in the state $|2,1,1\rangle$.

7.12 We cannot construct energy eigenstates of the hydrogen atom which separate in the coordinates $\boldsymbol{x}_e$ and $\boldsymbol{x}_p$ of the electron and the proton. If we want to have a representation which factorizes in electron and proton wave functions, the best we can do is to expand the energy eigenstates $\Psi_{\boldsymbol{K},n,\ell,m}(\boldsymbol{R},\boldsymbol{r})$ in terms of complete sets of functions $f_e(\boldsymbol{x}_e)g_p(\boldsymbol{x}_p)$ which arise from complete sets of functions $f(\boldsymbol{x})$, $g(\boldsymbol{x})$ for single particle states. Expand the ground state of a hydrogen atom with center of mass momentum $\hbar\boldsymbol{K}$,

$$\Psi_{\boldsymbol{K},1,0,0}(\boldsymbol{R},\boldsymbol{r}) = \frac{1}{\sqrt{2a}^3\pi^2}\exp\left(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R} - \frac{r}{a}\right)$$

in terms of the complete basis of factorized plane electron and proton waves,

$$\langle \boldsymbol{k}_e,\boldsymbol{k}_p|\boldsymbol{x}_e,\boldsymbol{x}_p\rangle = \frac{1}{(2\pi)^3}\exp(\mathrm{i}\boldsymbol{k}_e\cdot\boldsymbol{x}_e + \mathrm{i}\boldsymbol{k}_p\cdot\boldsymbol{x}_p)\,.$$

7.13 Suppose we force a hydrogen atom into a 1s type state

$$\psi(\boldsymbol{r},t) = \frac{1}{\sqrt{\pi b^3}}\exp(-r/b)\exp(-\mathrm{i}E_1 t/\hbar), \tag{7.71}$$

where

$$E_1 = -\frac{\mu e^4}{32\pi^2\epsilon_0^2\hbar^2} = -\frac{e^2}{8\pi\epsilon_0 a}$$

is the ground state energy of the hydrogen atom, but the length parameter b is *not* the Bohr radius a.

7.13a How do the expectation values for kinetic, potential and total energy in the state (7.71) compare to the corresponding values in the ground state of the unperturbed hydrogen atom?

7.13b How do we have to change the potential energy of the system to force the hydrogen atom into the state (7.71)? Show that the change in potential energy can be written as

$$\Delta V = \frac{\hbar^2}{\mu}\left(\frac{1}{a}-\frac{1}{b}\right)\left(\frac{1}{r}-\frac{1}{2a}-\frac{1}{2b}\right).$$

7.14 Solve the differential equation (6.2) for the harmonic oscillator not by the operator method, but by the same methods which we have used to solve the radial equation (7.49) for the hydrogen atom.

7.15 The proposal of Bohmian mechanics[10] asserts that quantum mechanics

[10] D. Bohm, Phys. Rev. 85, 166 & 180 (1952).

with the Born probability interpretation should be replaced by a pilot wave theory. The wave function would still satisfy the Schrödinger equation. However, instead of serving as a probability amplitude for the outcome of single measurements, the wave function provides a pilot wave for particles in the sense that an N particle wave function determines the velocity field for the particles through the equation

$$\frac{d\boldsymbol{x}_I(t)}{dt} = \frac{\hbar}{2\mathrm{i}m_I\,|\psi(\boldsymbol{x}_1(t),\ldots\boldsymbol{x}_N(t);t)|^2} \times \left(\psi^+(\boldsymbol{x}_1(t),\ldots\boldsymbol{x}_N(t);t)\overset{\leftrightarrow}{\boldsymbol{\nabla}}_I\psi(\boldsymbol{x}_1(t),\ldots\boldsymbol{x}_N(t);t)\right). \tag{7.72}$$

It has been claimed that this leads to predicitions which are indistinguishable from quantum mechanics, at least as long as we are only concerned with motion of non-relativistic particles.
We consider a hydrogen atom with center of mass velocity $\boldsymbol{V} = \hbar\boldsymbol{K}/(m_e+m_p)$. Which velocities would equation (7.72) predict for the velocities of the proton and the electron in the ground state of the atom? How would the proton and the electron then be arranged in the ground state of a hydrogen atom?

Solution

The ground state wave function in terms of electron and proton coordinates is

$$\langle\boldsymbol{x}_e,\boldsymbol{x}_p|1,0,0;\boldsymbol{K}(t)\rangle = \exp\left(\mathrm{i}\boldsymbol{K}\cdot\frac{m_e\boldsymbol{x}_e+m_p\boldsymbol{x}_p}{m_e+m_p}\right)\exp\left(-\frac{|\boldsymbol{x}_e-\boldsymbol{x}_p|}{a}\right) \times\frac{1}{\pi^2\sqrt{2a^3}}\exp\left(-\frac{\mathrm{i}\hbar}{2(m_e+m_p)}\boldsymbol{K}^2t-\frac{\mathrm{i}}{\hbar}E_1t\right).$$

Equation (7.72) then yields

$$\boldsymbol{v}_e = \boldsymbol{v}_p = \boldsymbol{V}.$$

This result agrees with the corresponding expectation values for particle velocities in quantum mechanics. However, here we assume that both the electron and the proton have well defined (although not individually observable) trajectories, and their velocities are sharply defined. Therefore the electron and the proton would both move with the constant center of mass velocity $\boldsymbol{V}$ along straight lines. Motion with a fixed distance between the two particles seems hardly compatible with their electromagnetic attraction, but Bohmian mechanics explains this in terms of an additional quantum potential generated by the wave function,

$$V_\psi(\boldsymbol{x}) = -\frac{\hbar^2}{2m|\psi(\boldsymbol{x})|}\Delta|\psi(\boldsymbol{x})|,$$

i.e. the wave function would also induce an additional force field in Bohmian mechanics.

However, motion with fixed sparation between the electron and the proton should imply observation of an electric dipole moment for individual hydrogen atoms, contrary to ordinary quantum mechanics.
On the other hand, motion of the electron and the proton right on top of each other is an appealing classical picture, but is incompatible with the positive nucleus plus negative electron hull structure of atoms that follows e.g. from the van der Waals equation of state for gases (which gives atomic radii between 1 and 2 Å) and Rutherford scattering (which tells us two things: only the positive charge is concentrated in the nucleus, and the nucleus has only a radius of a few femtometers).
To avoid this negative verdict, we might argue that we should rather consider a cold gas of Bohmian hydrogen atoms to understand the implications of the Bohmian interpretation for the ground state wave function.
In a cold gas of Bohmian hydrogen atoms the static distance between the electron and the proton would be distributed according to $|\langle \boldsymbol{x}_e - \boldsymbol{x}_p|1,0,0\rangle|^2$. There would be many hydrogen atoms with the electron sitting right on top of the proton, but there would also be a lot of hydrogen atoms with a large separation and a corresponding static electric dipole moment $\boldsymbol{d} = e(\boldsymbol{x}_p - \boldsymbol{x}_e)$. Standard quantum mechanics in Born's interpretation does not predict an electric dipole moment in any of the hydrogen atoms, because an electron would only appear to have a particular location if we specifically perform a measurement asking for the location. However, in Bohmian mechanics, the electron and proton would exist as particles at all times with fixed relative location, and therefore there should be an average dipole moment per atom in the ground state with magnitude $\langle|\boldsymbol{d}|\rangle = e\langle r\rangle = 3ea/2$.
These dipole moments might be randomly distributed and therefore we might not observe a macroscopic dipole moment. However, we could align these dipole moments with a weak static external electric field. The field strength would be much weaker than the internal field strength in hydrogen, to ensure that the ground state wave function is not perturbed. In addition to any induced electric dipole moment in the Bohmian hydrogen atoms (which would also exist in the same way for the standard quantum mechanical hydrogen atoms) there would be a macroscopic dipole moment from orientation polarization. This would be a real difference from the standard quantum mechanical cold hydrogen gas. Therefore I disagree with claims that Bohmian mechanics is just a different ontological interpretation of non-relativistic quantum mechanics. Trying to make pilot wave theories work is certainly tempting, but I cannot consider Bohmian mechanics as a serious competitor to standard quantum mechanics with the Born interpretation of quantum states.

Chapter 8

Spin and Addition of Angular Momentum Type Operators

We have seen in Section 7.5 that representations of the angular momentum Lie algebra (7.19) are labelled by a quantum number ℓ which can take half-integer or integer values. However, we have also seen in Section 7.6 that ℓ is limited to integer values when the operators $\boldsymbol{M}$ actually refer to angular momentum, because the wave functions[1] $\langle \boldsymbol{x}|n,\ell,m_\ell\rangle$ or $\langle \boldsymbol{x}|k,\ell,m_\ell\rangle$ for angular momentum eigenstates must be single valued. It was therefore very surprising when Stern, Gerlach, Goudsmit, Uhlenbeck and Pauli in the 1920s discovered that half-integer values of ℓ are also realized in nature, although in that case ℓ cannot be related to an angular momentum any more. Half-integer values of ℓ arise in nature because leptons and quarks carry a representation of the "covering group" SU(2) of the proper rotation group SO(3), where SU(2) stands for the group which can be represented by special unitary 2×2 matrices[2]. The designation "special" refers to the fact that the matrices are also required to have determinant 1. The generators of the groups SU(2) and SO(3) satisfy the same Lie algebra (7.19), but for every rotation matrix $\underline{R}(\boldsymbol{\varphi}) = \underline{R}(\boldsymbol{\varphi}+2\pi\hat{\boldsymbol{\varphi}})$ there are two unitary 2×2 matrices $\underline{U}(\boldsymbol{\varphi}) = -\underline{U}(\boldsymbol{\varphi}+2\pi\hat{\boldsymbol{\varphi}})$. In that sense SU(2) provides a double cover of SO(3).
We will use the notations $\boldsymbol{l}$ and $\boldsymbol{M}$ for angular momenta, and $\boldsymbol{s}$ or $\boldsymbol{S}$ for spins.

8.1 Spin and magnetic dipole interactions

A particle of charge q and mass m which moves with angular momentum $\boldsymbol{l}$ through a constant magnetic field $\boldsymbol{B}$ has its energy levels shifted through a Zeeman term in the Hamiltonian,

$$H = -\frac{q}{2m}\boldsymbol{l}\cdot\boldsymbol{B}. \tag{8.1}$$

[1] We denote the magnetic quantum number with m_ℓ in this chapter because m will denote the mass of a particle.

[2] Ultimately, all particles carry representations of the covering group SL(2,$\mathbb{C}$) of the group SO(1,3) of proper orthochronous Lorentz transformations, see Appendices B and H.

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We will explore the origin of this term in Chapter 18, but for now we can think of it as a magnetic dipole term with a dipole moment

$$\boldsymbol{\mu_l} = \frac{q}{2m}\boldsymbol{l}.$$

The relation between $\boldsymbol{\mu_l}$ and $\boldsymbol{l}$ can be motivated from electrodynamics, but is actually a consequence of the coupling of electromagnetic fields in the Schrödinger equation. We will see this in detail in Chapter 18.
The quantization $\langle \ell, m_\ell | l_z | \ell, m_\ell \rangle = \hbar m_\ell$ for angular momentum components in a fixed direction yields a Zeeman shift

$$\Delta E = -\frac{q\hbar}{2m} B m_\ell, \quad -\ell \leq m_\ell \leq \ell,$$

of the energy levels of a charged particle in a magnetic field. For orbital momentum the resulting number $2\ell + 1$ of energy levels is odd. However, the observation of motion of Ag atoms through an inhomogeneous field by Stern and Gerlach in 1921 revealed a split of energy levels of these atoms into two levels in a magnetic field. This complies with a split into $2s + 1$ levels only if the angular momentum like quantum number s is $1/2$. This additional angular momentum type quantum number is denoted as spin. Spin behaves in many respects similar to angular momentum, but it cannot be an orbital angular momentum because that would exclude half-integer values for s. Another major difference to angular momentum concerns the fact that the spectroscopically observed splitting of energy levels due to spin complies with a magnetic dipole type interaction only if the corresponding Zeeman type term is increased by a factor g_s,

$$H = -\boldsymbol{\mu_s} \cdot \boldsymbol{B}, \quad \boldsymbol{\mu_s} = g_s \frac{q}{2m}\boldsymbol{s}.$$

This "anomalous g factor" is in very good approximation $g_s \simeq 2$. The relation between $\boldsymbol{\mu_s}$ and $\boldsymbol{s}$ is a consequence of relativistic quantum mechanics and will be explained in Chapter 21.
The important observation for now is that there exist operators which satisfy the angular momentum Lie algebra (7.19),

$$[S_i, S_j] = \mathrm{i}\hbar\epsilon_{ijk} S_k,$$

and therefore have representations of the form (7.24-7.29),

$$S_z|s, m_s\rangle = \hbar m_s |s, m_s\rangle, \tag{8.2}$$

$$S_\pm|s, m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}\,|s, m_s \pm 1\rangle, \tag{8.3}$$

$$\boldsymbol{S}^2|s, m_s\rangle = \hbar^2 s(s+1)|s, m_s\rangle.$$

However, these operators are not related to orbital angular momentum and therefore can have half-integer values of the quantum number s in their representations.

Our previous calculations of matrix representations of the rotation group in Section 7.5 imply that spin is related to transformation properties of particle wave functions under rotations. However, before we can elaborate on this, we have to take a closer look at the representations with $s = 1/2$.
In the following mapping between matrices we use an index mapping for the magnetic quantum numbers $m_s = \pm 1/2$ to indices

$$a(m_s) = (3/2) - m_s, \tag{8.4}$$

i.e. $m_s = 1/2 \to a(m_s) = 1$, $m_s = -1/2 \to a(m_s) = 2$.
Substitution of $s = 1/2$ in equations (8.2, 8.3) yields

$$\langle 1/2, m'_s | S_3 | 1/2, m_s \rangle = \hbar m_s \delta_{m'_s, m_s} = \frac{\hbar}{2} (\sigma_3)_{a(m'_s), a(m_s)}, \tag{8.5}$$

$$\langle 1/2, m'_s | S_1 | 1/2, m_s \rangle = \frac{\hbar}{2} \left(\delta_{m'_s, m_s+1} + \delta_{m'_s, m_s-1} \right) = \frac{\hbar}{2} (\sigma_1)_{a(m'_s), a(m_s)}, \tag{8.6}$$

and

$$\langle 1/2, m'_s | S_2 | 1/2, m_s \rangle = \frac{\hbar}{2\mathrm{i}} \left(\delta_{m'_s, m_s+1} - \delta_{m'_s, m_s-1} \right) = \frac{\hbar}{2} (\sigma_2)_{a(m'_s), a(m_s)}, \tag{8.7}$$

with the Pauli matrices

$$\underline{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \underline{\sigma}_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \underline{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{8.8}$$

The Pauli matrices provide a basis for hermitian traceless 2×2 matrices and satisfy the relation

$$\underline{\sigma}_i \cdot \underline{\sigma}_j = \delta_{ij} 1 + \mathrm{i} \epsilon_{ijk} \underline{\sigma}_k. \tag{8.9}$$

The index mapping $m_s \to a(m_s)$ is employed in the notation of spin states as $|1/2, m_s\rangle \to |a(m_s)\rangle$ such that a general $s = 1/2$ state is

$$|\psi\rangle = \sum_{m_s=1/2}^{-1/2} |1/2, m_s\rangle \langle 1/2, m_s | \psi \rangle = \sum_{a=1}^{2} |a\rangle \langle a | \psi \rangle \tag{8.10}$$

Knowledge of a spin 1/2 state $|\psi\rangle$ is equivalent to the knowledge of its two components $\langle 1/2, 1/2 | \psi \rangle \equiv \langle 1 | \psi \rangle \equiv \psi_1$, $\langle 1/2, -1/2 | \psi \rangle \equiv \langle 2 | \psi \rangle \equiv \psi_2$. In column notation this corresponds to the *2-spinor* ψ

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, \tag{8.11}$$

such that application of a spin operator S_i

$$\langle 1/2, m_s | \psi' \rangle = \langle 1/2, m_s | S_i | \psi \rangle = \sum_{m'_s=1/2}^{-1/2} \langle 1/2, m_s | S_i | 1/2, m'_s \rangle \langle 1/2, m'_s | \psi \rangle$$

corresponds to the matrix multiplication

$$\psi' = \frac{\hbar}{2}\underline{\sigma}_i \cdot \psi. \tag{8.12}$$

For example, a general electron state $|\psi\rangle$ corresponds to a superposition of spin orientations $\pm 1/2$ and a superposition of $\boldsymbol{x}$ eigenstates,

$$|\psi\rangle = \int d^3\boldsymbol{x} \sum_{m_s=1/2}^{-1/2} |\boldsymbol{x}; m_s\rangle\langle \boldsymbol{x}; m_s|\psi\rangle \equiv \int d^3\boldsymbol{x} \sum_{m_s=1/2}^{-1/2} |\boldsymbol{x}; m_s\rangle \psi_{a(m_s)}(\boldsymbol{x}),$$

and is given in 2-spinor notation (listing all common index conventions) as

$$\psi(\boldsymbol{x}) = \begin{pmatrix} \psi_1(\boldsymbol{x}) \\ \psi_2(\boldsymbol{x}) \end{pmatrix} \equiv \begin{pmatrix} \psi_{1/2}(\boldsymbol{x}) \\ \psi_{-1/2}(\boldsymbol{x}) \end{pmatrix} \equiv \begin{pmatrix} \psi_+(\boldsymbol{x}) \\ \psi_-(\boldsymbol{x}) \end{pmatrix} \equiv \begin{pmatrix} \psi_\uparrow(\boldsymbol{x}) \\ \psi_\downarrow(\boldsymbol{x}) \end{pmatrix}. \tag{8.13}$$

The normalization is

$$\int d^3\boldsymbol{x} \left(|\psi_1(\boldsymbol{x})|^2 + |\psi_2(\boldsymbol{x})|^2 \right) = 1.$$

The probability densities for finding the electron with spin up or down in the location $\boldsymbol{x}$ are $|\psi_1(\boldsymbol{x})|^2$ and $|\psi_2(\boldsymbol{x})|^2$, respectively, while the probability density to find the electron in the location $\boldsymbol{x}$ in any spin orientation is $|\psi_1(\boldsymbol{x})|^2 + |\psi_2(\boldsymbol{x})|^2$. Note that these three probability densities can have maxima in three different locations, which reminds us how questionable the concept of a particle is in quantum mechanics.

8.2 Transformation of scalar, spinor, and vector wave functions under rotations

The commutation relations between angular momentum $\boldsymbol{M} = \mathbf{x} \times \mathbf{p}$ and $\mathbf{x}$,

$$[M_i, \mathrm{x}_j] = \mathrm{i}\hbar\epsilon_{ijk}\mathrm{x}_k$$

imply with the rotation generators $(L_i)_{jk} = \epsilon_{ijk}$ and the rotation matrices from Section 7.4

$$\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{M}\right)\mathbf{x}\exp\left(-\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{M}\right) = \exp(-\boldsymbol{\varphi}\cdot\boldsymbol{L})\cdot\boldsymbol{x} = \underline{R}(-\boldsymbol{\varphi})\cdot\mathbf{x},$$

and therefore

$$\langle\boldsymbol{x}|\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{M}\right) = \langle\underline{R}(-\boldsymbol{\varphi})\cdot\boldsymbol{x}|.$$

Rotation of a state

$$|\psi(t)\rangle \to |\psi'(t)\rangle = \exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{M}\right)|\psi(t)\rangle$$

therefore implies for the rotated wave function

$$\langle \boldsymbol{x}'|\psi'(t)\rangle = \langle \underline{R}(\boldsymbol{\varphi})\cdot\boldsymbol{x}|\psi'(t)\rangle = \langle \boldsymbol{x}|\psi(t)\rangle, \tag{8.14}$$

where

$$\boldsymbol{x}' = \underline{R}(\boldsymbol{\varphi})\cdot\boldsymbol{x}$$

is the rotated coordinate vector.
A transformation behavior like (8.14) tells us that the transformed wave function at the transformed set of coordinates is the same as the original wave function at the original set of coordinates. Such a transformation behavior is denoted as a *scalar* transformation law, and the corresponding wave functions are scalar functions.
On the other hand, spinor wave functions have two components which denote probability amplitudes for spin orientation along a given spatial axis, conventionally chosen as the z axis. The z' axis of the rotated frame will generically have a direction which is different from the z axis, and the probability amplitudes for spin along the z' direction will be different from the probability amplitudes along the z direction.
The rotated 2-spinor state

$$|\psi(t)\rangle \to |\psi'(t)\rangle = \exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\,(\boldsymbol{M}+\boldsymbol{S})\right)|\psi(t)\rangle \tag{8.15}$$

has components

$$\begin{aligned}\langle \boldsymbol{x}', a|\psi'(t)\rangle \equiv \psi'_a(\boldsymbol{x}',t) &= \langle \underline{R}(\boldsymbol{\varphi})\cdot\boldsymbol{x}, a|\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\,(\boldsymbol{M}+\boldsymbol{S})\right)|\psi(t)\rangle \\ &= \langle \boldsymbol{x}, a|\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\varphi}\cdot\boldsymbol{S}\right)|\psi(t)\rangle = \left[\exp\left(\frac{\mathrm{i}}{2}\boldsymbol{\varphi}\cdot\underline{\boldsymbol{\sigma}}\right)\right]_{ab}\langle \boldsymbol{x}, b|\psi(t)\rangle\end{aligned}$$

or in terms of the column 2-spinor (8.13),

$$\psi'(\boldsymbol{x}',t) = \exp\left(\frac{\mathrm{i}}{2}\boldsymbol{\varphi}\cdot\underline{\boldsymbol{\sigma}}\right)\cdot\psi(\boldsymbol{x},t). \tag{8.16}$$

For comparison, we also give the result if we use the representation (8.2,8.3) with $s=1$ for the spin operators $\boldsymbol{S}$ on wave functions. In that case the matrix correspondence

$$\langle s=1/2, m'_s|\boldsymbol{S}|s=1/2, m_s\rangle = \hbar\boldsymbol{\sigma}_{a(m'_s),a(m_s)}/2$$

is replaced in a first step by

$$\langle s=1, m'_s|\boldsymbol{S}|s=1, m_s\rangle = \hbar\boldsymbol{\Sigma}_{j(m'_s),j(m_s)}$$

with $j(m_s) = 2 - m_s$,

$$\underline{\Sigma}_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \underline{\Sigma}_2 = \frac{\mathrm{i}}{\sqrt{2}}\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix},$$
$$\underline{\Sigma}_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{8.17}$$

However, this is still not the standard matrix representation for spin $s = 1$. The connection with the conventional representation (7.16) of vector rotation operators is achieved through the similarity transformation

$$\underline{\boldsymbol{L}} = \frac{\mathrm{i}}{\hbar}\underline{M} = \mathrm{i}\underline{A} \cdot \underline{\boldsymbol{\Sigma}} \cdot \underline{A}^{-1} \tag{8.18}$$

with the unitary matrix

$$\underline{A} = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 & 0 & 1 \\ -\mathrm{i} & 0 & -\mathrm{i} \\ 0 & \sqrt{2} & 0 \end{pmatrix}, \quad \underline{A}^{-1} = \frac{1}{\sqrt{2}}\begin{pmatrix} -1 & \mathrm{i} & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & \mathrm{i} & 0 \end{pmatrix}.$$

The transformation law for *vector wave functions* $\langle \boldsymbol{x}, i|A(t)\rangle \equiv A_i(\boldsymbol{x}, t)$ under rotations is then given in terms of the same rotation matrices $\underline{R}(\boldsymbol{\varphi}) = \exp(\boldsymbol{\varphi} \cdot \underline{\boldsymbol{L}})$ which effect rotations of the vector $\boldsymbol{x}$,

$$\boldsymbol{x}' = \exp(\boldsymbol{\varphi} \cdot \underline{\boldsymbol{L}}) \cdot \boldsymbol{x}, \quad \boldsymbol{A}'(\boldsymbol{x}', t) = \exp(\boldsymbol{\varphi} \cdot \underline{\boldsymbol{L}}) \cdot \boldsymbol{A}(\boldsymbol{x}, t). \tag{8.19}$$

We will see in Chapter 18 that photons are described by vector wave functions.

8.3 Addition of angular momentum like quantities

In classical mechanics, angular momentum is an additive vector quantity which is conserved in rotationally symmetric systems. Furthermore, the transformation equation (8.15) for spinor states involved addition of two different operators which both satisfy the angular momentum Lie algebra (7.19). However, before immersing ourselves into the technicalities of how angular momentum type operators are combined in quantum mechanics, it is worthwhile to point out that interactions in atoms and materials provide another direct physical motivation for addition of angular momentum like quantities.

We have seen in Section 7.1 that relative motion of two interacting particles with an interaction potential $V(\boldsymbol{x}_1 - \boldsymbol{x}_2)$ can be described in terms of effective single particle motion of a (quasi-)particle with location $\boldsymbol{r}(t) = \boldsymbol{x}_1(t) - \boldsymbol{x}_2(t)$, mass $m = m_1 m_2/(m_1 + m_2)$, momentum $\boldsymbol{p} = (m_2\boldsymbol{p}_1 - m_1\boldsymbol{p}_2)/(m_1 + m_2)$ and angular momentum $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$.

Furthermore, if $m_2 \gg m_1$, but the charge q_2 is not much larger than q_1 and the spin $|\boldsymbol{s}_2|$ is not much larger than $|\boldsymbol{s}_1|$, then we can assign a charge[3] $q = q_1$ and a spin $\boldsymbol{s} = \boldsymbol{s}_1$ to the quasi-particle with mass $m \simeq m_1$.
A particle of charge $-e$ and mass m with angular momentum operators $\boldsymbol{l}$ and spin $\boldsymbol{s}$ experiences a contribution to its energy levels from an interaction term

$$H_{\boldsymbol{l}\cdot\boldsymbol{s}} = \frac{\mu_0 e^2}{8\pi m^2 r^3}\boldsymbol{l}\cdot\boldsymbol{s} \tag{8.20}$$

in its Hamiltonian, if it is moving in the electric field $\boldsymbol{E} = \hat{\boldsymbol{r}}e/(4\pi\epsilon_0 r^2)$ of a much heavier particle of charge e. One can think of $H_{\boldsymbol{l}\cdot\boldsymbol{s}}$ as a magnetic dipole-dipole interaction $(\mu_0/4\pi r^3)\boldsymbol{\mu}_{\boldsymbol{l}}\cdot\boldsymbol{\mu}_{\boldsymbol{s}}$, but finally it arises as a consequence of a relativistic generalization of the Schrödinger equation. We will see this in Chapter 21. However, for the moment we simply accept the existence of terms like (8.20) as an experimental fact. These terms contribute to the fine structure of spectral lines. The term (8.20) is known as a *spin-orbit coupling* term or ls coupling term, and pertains in this particular form to the energy levels of the quasi-particle which describes relative motion in a two-particle system. However, if there are many charged particles like in a many electron atom, then there will also be interaction terms between angular momenta and spins of different particles in the system, i.e. we will have terms of the form

$$H_{\boldsymbol{j}_1\cdot\boldsymbol{j}_2} = f(r_{12})\boldsymbol{j}_1\cdot\boldsymbol{j}_2, \tag{8.21}$$

where $\boldsymbol{j}_i$ are angular momentum like operators. We will superficially denote all these operators (including spin) simply as angular momentum operators in the following.
Diagonalization of Hamiltonians like (8.20) or (8.21) requires us to combine two operators to a new operator according to $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$ or $\boldsymbol{j} = \boldsymbol{j}_1 + \boldsymbol{j}_1$, respectively. From the perspective of spectroscopy, terms like (8.20) or (8.21) are the very reason why we have to know how to combine two angular momentum type operators in quantum mechanics. Diagonalization of (8.20) and (8.21) is important for understanding the spectra of atoms and molecules, and spin-orbit coupling also affects energy levels in materials. Furthermore, Hamiltonians of the form $-2J\boldsymbol{s}_1\cdot\boldsymbol{s}_2$ provide an effective description of interactions in magnetic materials, see Chapter 17, and they are important for spin entanglement, decoherence, and spintronics. The advantage of introducing the combined angular momentum operator $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$ is that it also satisfies angular momentum commutation rules (7.19) $[j_a, j_b] = \mathrm{i}\hbar\epsilon_{abc}j_c$ and therefore should have eigenstates $|j, m_j\rangle$,

$$\boldsymbol{j}^2|j,m_j\rangle = \hbar^2 j(j+1)|j,m_j\rangle, \quad j_z|j,m_j\rangle = \hbar m_j|j,m_j\rangle. \tag{8.22}$$

However, $\boldsymbol{j}$ commutes with $\boldsymbol{l}^2$ and $\boldsymbol{s}^2$, $[j_a, \boldsymbol{l}^2] = [j_a, \boldsymbol{s}^2] = 0$, and therefore we can try to construct the states in (8.22) such that they also satisfy the

[3] We will return to the question of assignment of charge and spin to the quasi-particle for relative motion in Chapter 18.

properties

$$\boldsymbol{l}^2|j,m_j,\ell,s\rangle = \hbar^2\ell(\ell+1)|j,m_j,\ell,s\rangle,$$
$$\boldsymbol{s}^2|j,m_j,\ell,s\rangle = \hbar^2 s(s+1)|j,m_j,\ell,s\rangle.$$

The advantage of these states is that they are eigenstates of the coupling operator (8.20),

$$\begin{aligned}\boldsymbol{l}\cdot\boldsymbol{s}|j,m_j,\ell,s\rangle &= \frac{\boldsymbol{j}^2-\boldsymbol{l}^2-\boldsymbol{s}^2}{2}|j,m_j,\ell,s\rangle \\ &= \hbar^2\frac{j(j+1)-\ell(\ell+1)-s(s+1)}{2}|j,m_j,\ell,s\rangle\end{aligned}$$

and therefore the energy shifts from spin-orbit coupling in these states are

$$\Delta E = \frac{\mu_0 e^2\hbar^2}{16\pi m^2}\langle r^{-3}\rangle\left[j(j+1)-\ell(\ell+1)-s(s+1)\right]. \tag{8.23}$$

The states that we know for the operators $\boldsymbol{l}$ and $\boldsymbol{s}$ are the eigenstates $|\ell,m_\ell\rangle$ for $\boldsymbol{l}^2$ and l_z, and $|s,m_s\rangle$ for $\boldsymbol{s}^2$ and s_z, respectively. We can combine these states into states

$$|\ell,m_\ell\rangle\otimes|s,m_s\rangle \equiv |\ell,m_\ell;s,m_s\rangle \tag{8.24}$$

which will be denoted as a tensor product basis of anglar momentum states. The understanding in the tensor product notation is that $\boldsymbol{l}$ only acts on the first factor and $\boldsymbol{s}$ only on the second factor. Strictly speaking the combined angular momentum operator should be written as

$$\boldsymbol{j} = \boldsymbol{l}\otimes 1 + 1\otimes\boldsymbol{s},$$

which automatically ensures the correct rule

$$\boldsymbol{j}(|\ell,m_\ell\rangle\otimes|s,m_s\rangle) = \boldsymbol{l}|\ell,m_\ell\rangle\otimes|s,m_s\rangle + |\ell,m_\ell\rangle\otimes\boldsymbol{s}|s,m_s\rangle,$$

but we will continue with the standard physics notation $\boldsymbol{j}=\boldsymbol{l}+\boldsymbol{s}$.
The main problem for combination of angular momenta is how to construct the eigenstates $|j,m_j,\ell,s\rangle$ for total angular momentum from the tensor products (8.24) of eigenstates of the initial angular momenta,

$$|j,m_j,\ell,s\rangle = \sum_{m_\ell,m_s}|\ell,m_\ell;s,m_s\rangle\langle\ell,m_\ell;s,m_s|j,m_j,\ell,s\rangle. \tag{8.25}$$

We will denote the states $|j,m_j,\ell,s\rangle$ as the combined angular momentum states.
There is no summation over indices $\ell'\neq\ell$ or $s'\neq s$ on the right hand side because all states involved are eigenstates of $\boldsymbol{l}^2$ and $\boldsymbol{s}^2$ with the same eigenvalues $\hbar^2\ell(\ell+1)$ or $\hbar^2 s(s+1)$, respectively.
The components $\langle\ell,m_\ell;s,m_s|j,m_j,\ell,s\rangle$ of the transformation matrix from the initial angular momenta states to the combined angular momentum states are

known as Clebsch-Gordan coefficients or vector addition coefficients. The notation $\langle \ell, m_\ell; s, m_s | j, m_j, \ell, s\rangle$ is logically satisfactory by explicitly showing that the Clebsch-Gordan coefficients can also be thought of as the representation of the combined angular momentum states $|j, m_j, \ell, s\rangle$ in the basis of tensor product states $|\ell, m_\ell; s, m_s\rangle$. However, the notation is also redundant in terms of the quantum numbers ℓ and s, and a little clumsy. It is therefore convenient to abbreviate the notation slightly by setting

$$\langle \ell, m_\ell; s, m_s | j, m_j, \ell, s\rangle \equiv \langle \ell, m_\ell; s, m_s | j, m_j\rangle.$$

The new angular momentum eigenstates must also be normalizable and orthogonal for different eigenvalues, i.e. the transformation matrix must be unitary,

$$\sum_{m_\ell, m_s} \langle j, m_j | \ell, m_\ell; s, m_s\rangle \langle \ell, m_\ell; s, m_s | j', m'_j\rangle = \delta_{j,j'}\delta_{m_j,m'_j}, \tag{8.26}$$

$$\sum_{j,m_j} \langle \ell, m_\ell; s, m_s | j, m_j\rangle \langle j, m_j | \ell, m'_\ell; s, m'_s\rangle = \delta_{m_\ell,m'_\ell}\delta_{m_s,m'_s}. \tag{8.27}$$

The hermiticity properties

$$j_z = (l_z + s_z)^+, \quad j_\pm = (l_\mp + s_\mp)^+$$

imply with the definition (4.25) of adjoint operators the relations

$$m_j \langle \ell, m_\ell; s, m_s | j, m_j\rangle = (m_\ell + m_s)\, \langle \ell, m_\ell; s, m_s | j, m_j\rangle \tag{8.28}$$

and

$$\begin{aligned} &\sqrt{j(j+1) - m_j(m_j \pm 1)}\langle \ell, m_\ell; s, m_s | j, m_j \pm 1\rangle \\ &= \sqrt{\ell(\ell+1) - m_\ell(m_\ell \mp 1)}\langle \ell, m_\ell \mp 1; s, m_s | j, m_j\rangle \\ &\quad + \sqrt{s(s+1) - m_s(m_s \mp 1)}\langle \ell, m_\ell; s, m_s \mp 1 | j, m_j\rangle. \end{aligned} \tag{8.29}$$

Equation (8.28) yields

$$\langle \ell, m_\ell; s, m_s | j, m_j\rangle = \delta_{m_\ell+m_s,m_j} \langle \ell, m_\ell; s, m_s | j, m_\ell + m_s\rangle.$$

The highest occuring value of m_j which is also the highest occuring value for j is therefore $\ell + s$, and there is only one such state. This determines the state $|\ell + s, \ell + s, \ell, s\rangle$ up to a phase factor to

$$|\ell + s, \ell + s, \ell, s\rangle = |\ell, \ell; s, s\rangle, \tag{8.30}$$

i.e. we choose the phase factor as

$$\langle \ell, \ell; s, s | \ell + s, \ell + s\rangle = 1.$$

Repeated application of $j_- = l_- + s_-$ on the state (8.30) then yields all the remaining states of the form $|\ell + s, m_j, \ell, s\rangle$ or equivalently the remaining

Clebsch-Gordan coefficients of the form $\langle \ell, m_\ell; s, m_s | \ell + s, m_j = m_\ell + m_s \rangle$ with $-\ell - s \leq m_j < \ell + s$. For example, the next two lower states with $j = \ell + s$ are given by

$$\begin{aligned} j_- |\ell + s, \ell + s, \ell, s\rangle &= \sqrt{2(\ell + s)} |\ell + s, \ell + s - 1, \ell, s\rangle \\ &= \sqrt{2\ell} |\ell, \ell - 1; s, s\rangle + \sqrt{2s} |\ell, \ell; s, s - 1\rangle, \end{aligned}$$

$$\begin{aligned} j_-^2 |\ell + s, \ell + s, \ell, s\rangle &= 2\sqrt{\ell + s}\sqrt{2(\ell + s) - 1} |\ell + s, \ell + s - 2, \ell, s\rangle \\ &= 2\sqrt{\ell(2\ell - 1)} |\ell, \ell - 2; s, s\rangle + 4\sqrt{\ell s} |\ell, \ell - 1; s, s - 1\rangle \\ &\quad + 2\sqrt{s(2s - 1)} |\ell, \ell; s, s - 2\rangle. \end{aligned} \tag{8.31}$$

However, we have two states in the $|\ell, m_\ell; s, m_s\rangle$ basis with total magnetic quantum number $\ell + s - 1$, but so far discovered only one state in the $|j, m_j, \ell, s\rangle$ basis with this magnetic quantum number. We can therefore construct a second state with $m_j = \ell + s - 1$, which is orthogonal to the state $|\ell + s, \ell + s - 1, \ell, s\rangle$,

$$|\ell + s - 1, \ell + s - 1, \ell, s\rangle = \sqrt{\frac{s}{\ell + s}} |\ell, \ell - 1; s, s\rangle - \sqrt{\frac{\ell}{\ell + s}} |\ell, \ell; s, s - 1\rangle. \tag{8.32}$$

Application of $\boldsymbol{j}^2$ would show that this state has $j = \ell + s - 1$, which was already anticipated in the notation. Repeated application of the lowering operator j_- on this state would then yield all remaining states of the form $|\ell + s - 1, m_j, \ell, s\rangle$ with $1 - \ell - s \leq m_j < \ell + s - 1$, e.g.

$$\begin{aligned} &\sqrt{\ell + s - 1} |\ell + s - 1, \ell + s - 2, \ell, s\rangle = \sqrt{s \frac{2\ell - 1}{\ell + s}} |\ell, \ell - 2; s, s\rangle \\ &- \sqrt{\ell \frac{2s - 1}{\ell + s}} |\ell, \ell; s, s - 2\rangle + \frac{s - \ell}{\sqrt{\ell + s}} |\ell, \ell - 1; s - 1, s\rangle. \end{aligned} \tag{8.33}$$

We have three states with $m_j = \ell + s - 2$ in the direct product basis, viz. $|\ell, \ell - 2; s, s\rangle$, $|\ell, \ell; s, s - 2\rangle$ and $|\ell, \ell - 1; s - 1, s\rangle$, but so far we have only constructed two states in the combined angular momentum basis with $m_j = \ell + s - 2$, viz. $|\ell + s, \ell + s - 2, \ell, s\rangle$ and $|\ell + s - 1, \ell + s - 2, \ell, s\rangle$. We can therefore construct a third state in the combined angular momentum basis which is orthogonal to the other two states,

$$\begin{aligned} &|\ell + s - 2, \ell + s - 2, \ell, s\rangle \propto |\ell, \ell - 1; s - 1, s\rangle \\ &- |\ell + s, \ell + s - 2, \ell, s\rangle \langle \ell + s, \ell + s - 2, \ell, s | \ell, \ell - 1; s - 1, s\rangle \\ &- |\ell + s - 1, \ell + s - 2, \ell, s\rangle \langle \ell + s - 1, \ell + s - 2, \ell, s | \ell, \ell - 1; s - 1, s\rangle. \end{aligned}$$

Substitution of the states and Clebsch-Gordan coefficients from (8.31) and

(8.33) and normalization yields

$$|\ell+s-2,\ell+s-2,\ell,s\rangle = \sqrt{\frac{(2\ell-1)(2s-1)}{(2\ell+2s-1)(\ell+s-1)}}|\ell,\ell-1;s-1,s\rangle - \frac{\sqrt{s(2s-1)}}{\sqrt{(2\ell+2s-1)(\ell+s-1)}}|\ell,\ell-2;s,s\rangle + \frac{\sqrt{\ell(2\ell-1)}}{\sqrt{(2\ell+2s-1)(\ell+s-1)}}|\ell,\ell;s,s-2\rangle. \tag{8.34}$$

Application of j_- then yields the remaining states of the form $|\ell+s-2,m_j,\ell,s\rangle$. This process of repeated applications of j_- and forming new states with lower j through orthogonalization to the higher j states terminates when j reaches a minimal value $j=|\ell-s|$, when all $(2\ell+1)(2s+1)$ states $|\ell,m_\ell;s,m_s\rangle$ have been converted into the same number of states of the form $|j,m_j,\ell,s\rangle$.
This is a lengthy procedure when the number of states $(2\ell+1)(2s+1)$ is large, and the reader will certainly appreciate that Wigner [40] and Racah[4] have derived expressions for general Clebsch-Gordan coefficients. Racah derived in particular the following expression (see also [8,32])

$$\langle \ell,m_\ell;s,m_s|j,m_j\rangle = \delta_{m_\ell+m_s,m_j} \times \sum_{\nu=\nu_1}^{\nu_2}(-)^\nu \left(\frac{\sqrt{(2j+1)\cdot(\ell+s-j)!\cdot(j+\ell-s)!\cdot(j+s-\ell)!}}{\sqrt{(j+\ell+s+1)!}\cdot\nu!\cdot(\ell-m_\ell-\nu)!\cdot(s+m_s-\nu)!} \times \frac{\sqrt{(\ell+m_\ell)!\cdot(\ell-m_\ell)!\cdot(s+m_s)!\cdot(s-m_s)!\cdot(j+m_j)!\cdot(j-m_j)!}}{(j-s+m_\ell+\nu)!\cdot(j-\ell-m_s+\nu)!\cdot(\ell+s-j-\nu)!} \right). \tag{8.35}$$

The boundaries of the summation are determined by the requirements

$$\max[0,s-m_\ell-j,\ell+m_s-j] \le \nu \le \min[\ell+s-j,\ell-m_\ell,s+m_s].$$

Even if we decide to follow the standard convention of using real Clebsch-Gordan coefficients, there are still sign ambiguities for every particular value of j in $|\ell-s| \le j \le \ell+s$. This arises from the ambiguity of constructing the next orthogonal state when going from completed sets of states $|j',m_{j'},\ell,s\rangle$, $j<j'\le \ell+s$ to the next lower level j, because a sign ambiguity arises in the construction of the next orthogonal state $|j,j,\ell,s\rangle$. For example, Racah's formula (8.35) would give us the state $|\ell+s-2,\ell+s-2,\ell,s\rangle$ constructed before in equation (8.34), but with an overall minus sign.
Tables of Clebsch-Gordan coefficients had been compiled in the olden days, but nowadays these coefficients are implemented in commercial mathematical software programs for numerical and symbolic calculation, and there are also free online applets for the calculation of Clebsch-Gordan coefficients.

[4] G. Racah, Phys. Rev. 62, 438 (1942).

8.4 Problems

8.1 Calculate the spinor rotation matrix

$$\underline{U}(\boldsymbol{\varphi}) = \exp\left(\frac{\mathrm{i}}{2}\boldsymbol{\varphi}\cdot\underline{\boldsymbol{\sigma}}\right).$$

Hint: Use the expansion of the exponential function and consider odd and even powers of the exponent separately.
Verify the property

$$\underline{U}(\boldsymbol{\varphi}) = -\underline{U}(\boldsymbol{\varphi} + 2\pi\hat{\boldsymbol{\varphi}}).$$

8.2 We perform a rotation of the reference frame by an angle φ around the x-axis. How does this change the coordinates of the vector $\boldsymbol{x}$? Suppose we have a spinor which has only a spin up component in the old reference frame. How large are the spin up and spin down components of the spinor with respect to the rotated z axis?

8.3 The Cartesian coordinates $\{x, y, z\}$ transform under rotations according to

$$\boldsymbol{x} \to \boldsymbol{x}' = \exp\left(\boldsymbol{\varphi}\cdot\underline{\boldsymbol{L}}\right)\cdot\boldsymbol{x}.$$

Construct coordinates $\{X, Y, Z\}$ which transform with the matrices (8.17) under rotations,

$$\boldsymbol{X} \to \boldsymbol{X}' = \exp\left(\mathrm{i}\boldsymbol{\varphi}\cdot\underline{\boldsymbol{\Sigma}}\right)\cdot\boldsymbol{X}.$$

8.4 Construct the matrices $\langle s, m_s'|\boldsymbol{S}|s, m_s\rangle = \hbar\boldsymbol{\Sigma}_{j(m_s'),j(m_s)}$ for $s = 3/2$. Choose the index mapping $m_s \to j(m_s)$ such that

$$\underline{\Sigma}_3 = \frac{1}{2}\begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}.$$

Suppose we have an excited Lithium atom in a spin $s = 3/2$ state $\Psi_j(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3)$, $1 \le j \le 4$. How does this wave function transform under a rotation around the x axis by an angle $\varphi = \pi/2$?

8.5 Construct all the states $|j, m_j, \ell = 1, s = 1/2\rangle$ as linear combinations of the tensor product states $|\ell = 1, m_\ell; s = 1/2, m_s\rangle$, using either the recursive construction from the state $|j = 3/2, m_j = 3/2, \ell = 1, s = 1/2\rangle = |\ell = 1, m_\ell = 1; s = 1/2, m_s = 1/2\rangle$ or Racah's formula (8.35). Compare with the results from a symbolic computation program or an online applet for the calculation of Clebsch-Gordan coefficients.

Chapter 9

Stationary Perturbations in Quantum Mechanics

We denote a quantum system with a time-independent Hamiltonian H_0 as *solvable* (or sometimes also as *exactly solvable*) if we can calculate the energy eigenvalues and eigenstates of H_0 analytically. The harmonic oscillator and the hydrogen atom provide two examples of solvable quantum systems. Exactly solvable systems provide very useful models for quantum behavior in physical systems. The harmonic oscillator describes systems near a stable equilibrium, while the Hamiltonian with a Coulomb potential is an important model system for atomic physics and for every quantum system which is dominated by Coulomb interactions. However, in many cases the Schrödinger equation will not be solvable, and we have to go beyond solvable model systems to calculate quantitative properties. In these cases we have to resort to the calculation of approximate solutions. The methods developed in the present chapter are applicable to perturbations of discrete energy levels by time-independent perturbations V of the Hamiltonian, $H_0 \to H = H_0 + V$.

9.1 Time-independent perturbation theory without degeneracies

We consider a perturbation of a solvable time-independent Hamiltonian H_0 by a time-independent term V, and for book keeping purposes we extract a coupling constant λ from the perturbation,

$$H = H_0 + V \to H = H_0 + \lambda V.$$

After the relevant expressions for shifts of states and energy levels have been calculated to the desired order in λ, we usually subsume λ again in V, such that e.g. $\lambda\langle\phi^{(0)}|V|\psi^{(0)}\rangle \to \langle\phi^{(0)}|V|\psi^{(0)}\rangle$.
We know the unperturbed energy levels and eigenstates of the solvable Hamiltonian H_0,

$$H_0|\psi_j^{(0)}\rangle = E_j^{(0)}|\psi_j^{(0)}\rangle.$$

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In the present section we assume that the energy levels $E_j^{(0)}$ are not degenerate, and we want to calculate in particular approximations for the energy level E_i which arises from the unperturbed energy level $E_i^{(0)}$ due to the presence of the perturbation V. We will see below that consistency of the formalism requires that the differences $|E_i^{(0)} - E_j^{(0)}|$ for $j \neq i$ must have a positive minimal value, i.e. the unperturbed energy level $E_i^{(0)}$ for which we want to calculate corrections has to be discrete[1].
Orthogonality of eigenstates for different energy eigenvalues implies

$$\langle \psi_i^{(0)} | \psi_j^{(0)} \rangle = \delta_{ij}.$$

In the most common form of time-independent perturbation theory we try to find an approximate solution to the equation

$$H|\psi_i\rangle = E_i|\psi_i\rangle$$

in terms of power series expansions in the coupling constant λ,

$$|\psi_i\rangle = \sum_{n\geq 0} \lambda^n |\psi_i^{(n)}\rangle, \quad \langle \psi_i^{(0)} | \psi_i^{(n\geq 1)} \rangle = 0, \quad E_i = \sum_{n\geq 0} \lambda^n E_i^{(n)}. \tag{9.1}$$

Depending on the properties of V, these series may converge for small values of $|\lambda|$, or they may only hold as asymptotic expansions for $|\lambda| \to 0$. The book by Kato [19] provides results and resources on convergence and applicability properties of the perturbation series. Here we will focus on the commonly used first and second order expressions for wave functions and energy levels.
We can require

$$\langle \psi_i^{(0)} | \psi_i^{(n)} \rangle = \delta_{n,0} \tag{9.2}$$

because the recursion equation (9.3) below, which is derived without the assumption (9.2), does not determine these particular coefficients. One way to understand this is to observe that we can decompose $|\psi_i^{(n\geq 1)}\rangle$ into terms parallel and orthogonal to $|\psi_i^{(0)}\rangle$,

$$|\psi_i^{(n\geq 1)}\rangle = |\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|\psi_i^{(n\geq 1)}\rangle + |\psi_i^{(n\geq 1)}\rangle - |\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|\psi_i^{(n\geq 1)}\rangle.$$

Inclusion of the parallel part $|\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|\psi_i^{(n\geq 1)}\rangle$ in the zeroth order term, followed by a rescaling by

$$\left(1 + \langle \psi_i^{(0)} | \psi_i^{(n\geq 1)} \rangle\right)^{-1} = 1 - \langle \psi_i^{(0)} | \psi_i^{(n\geq 1)} \rangle + \mathcal{O}(\lambda^{2n})$$

to restore a coefficient 1 in the zeroth order term, affects only terms of order λ^{n+1} or higher in the perturbation series. This implies that if we have solved the Schrödinger equation to order λ^{n-1} with the constraint

$$\langle \psi_i^{(0)} | \psi_i^{(m)} \rangle = \delta_{m,0}, \quad 0 \leq m \leq n-1,$$

[1] This condition is not affected by a possible degeneracy of $E_i^{(0)}$, as will be shown in Section 9.2.

then ensuring that constraint also to order λ^n preserves the constraint for the lower order terms. Therefore we can fulfill the constraint (9.2) to any desired order in which we wish to calculate the perturbation series.
Substitution of the perturbative expansions into the Schrödinger equation $H|\psi_i\rangle = E_i|\psi_i\rangle$ yields

$$\sum_{n\geq 0}\lambda^n H_0|\psi_i^{(n)}\rangle + \sum_{n\geq 0}\lambda^{n+1}V|\psi_i^{(n)}\rangle = \sum_{m,n\geq 0}\lambda^{m+n}E_i^{(m)}|\psi_i^{(n)}\rangle$$
$$= \sum_{n\geq 0}\sum_{m=0}^{n}\lambda^n E_i^{(m)}|\psi_i^{(n-m)}\rangle.$$

This equation is automatically fulfilled at zeroth order. Isolation of terms of order λ^{n+1} for $n \geq 0$ yields

$$H_0|\psi_i^{(n+1)}\rangle + V|\psi_i^{(n)}\rangle = \sum_{m=0}^{n+1}E_i^{(m)}|\psi_i^{(n-m+1)}\rangle,$$

and projection of this equation onto $|\psi_j^{(0)}\rangle$ yields

$$E_j^{(0)}\langle\psi_j^{(0)}|\psi_i^{(n+1)}\rangle + \langle\psi_j^{(0)}|V|\psi_i^{(n)}\rangle = \sum_{m=0}^{n}E_i^{(m)}\langle\psi_j^{(0)}|\psi_i^{(n-m+1)}\rangle + E_i^{(n+1)}\delta_{ij}. \tag{9.3}$$

We can first calculate the first order corrections for energy levels and wave functions from this equation, and then solve it recursively to any desired order.

First order corrections to the energy levels and eigenstates

The first order corrections are found from equation (9.3) for $n = 0$. Substitution of $j = i$ implies for the first order shifts of the energy levels the result

$$E_i^{(1)} = \langle\psi_i^{(0)}|V|\psi_i^{(0)}\rangle, \tag{9.4}$$

and $j \neq i$ yields with $E_i^{(0)} \neq E_j^{(0)}$ the first order shifts of the energy eigenstates

$$\langle\psi_j^{(0)}|\psi_i^{(1)}\rangle = \frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}}. \tag{9.5}$$

Recursive solution of equation (9.3) for $n \geq 1$

We first observe that $j = i$ in equation (9.3) implies with the condition (9.2)

$$E_i^{(n+1)} = \langle\psi_i^{(0)}|V|\psi_i^{(n)}\rangle - \sum_{m=1}^{n}E_i^{(m)}\langle\psi_i^{(0)}|\psi_i^{(n-m+1)}\rangle = \langle\psi_i^{(0)}|V|\psi_i^{(n)}\rangle, \tag{9.6}$$

and $i \neq j$ yields

$$\left(E_i^{(0)} - E_j^{(0)}\right) \langle \psi_j^{(0)} | \psi_i^{(n+1)} \rangle = \langle \psi_j^{(0)} | V | \psi_i^{(n)} \rangle - \sum_{m=1}^{n} E_i^{(m)} \langle \psi_j^{(0)} | \psi_i^{(n-m+1)} \rangle. \tag{9.7}$$

The right hand sides of both equations depend only on lower order shifts of energy levels and eigenstates. Therefore these equations can be used for the recursive solution of equation (9.3) to arbitrary order.

Second order corrections to the energy levels and eigenstates

Substitution of $n = 1$ into equation (9.6) yields with (9.5) and

$$\sum\!\!\!\!\!\!\int_k |\psi_k^{(0)}\rangle\langle\psi_k^{(0)}| = 1$$

the second order shift

$$E_i^{(2)} = \sum\!\!\!\!\!\!\int_{k\neq i} \frac{\langle \psi_i^{(0)} | V | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | V | \psi_i^{(0)} \rangle}{E_i^{(0)} - E_k^{(0)}} = \sum\!\!\!\!\!\!\int_{k\neq i} \frac{|\langle \psi_i^{(0)} | V | \psi_k^{(0)} \rangle|^2}{E_i^{(0)} - E_k^{(0)}}. \tag{9.8}$$

States in the continuous part of the spectrum of H_0 will also contribute to the shifts in energy levels and eigenstates. It is only required that the energy level $E_i^{(0)}$, for which we want to calculate the corrections, is discrete.
Note that equation (9.8) implies that the second order correction to the ground state energy is always negative.
For the eigenstates, equation (9.7) yields with the first order results (9.4, 9.5) the equation (recall $i \neq j$ in (9.7))

$$\begin{aligned} \langle \psi_j^{(0)} | \psi_i^{(2)} \rangle = & \sum\!\!\!\!\!\!\int_{k\neq i} \frac{\langle \psi_j^{(0)} | V | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | V | \psi_i^{(0)} \rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)\left(E_i^{(0)} - E_k^{(0)}\right)} \\ & - \frac{\langle \psi_i^{(0)} | V | \psi_i^{(0)} \rangle \langle \psi_j^{(0)} | V | \psi_i^{(0)} \rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)^2}. \end{aligned} \tag{9.9}$$

Now we can explain why it is important that our original unperturbed energy level $E_i^{(0)}$ is discrete. To ensure that the n-th order corrections to the energy levels and eigenstates in equations (9.1) are really of order λ^n (or smaller than all previous terms), the matrix elements $|\langle \psi_j^{(0)} | V | \psi_k^{(0)} \rangle|$ of the perturbation operator should be at most of the same order of magnitude as the energy differences $|E_i^{(0)} - E_j^{(0)}|$ between the unperturbed level $E_i^{(0)}$ and the other unperturbed energy levels in the system. This implies in particular that the minimal absolute energy difference between $E_i^{(0)}$ and the other unperturbed energy levels must not vanish, i.e. $E_i^{(0)}$ must be a discrete energy level.

Equations (9.4) and (9.8) (and their counterparts (9.16) and (9.24) in degenerate perturbation theory below) used to be the most frequently employed equations of time-independent perturbation theory, because historically many experiments were concerned with spectroscopic determinations of energy levels. However, measurements e.g. of local electron densities or observations of wave functions (e.g. in scanning tunneling microscopes or through X-ray scattering using synchrotrons) are very common nowadays, and therefore the corrections to the states are also directly relevant for the interpretation of experimental data.

Summary of non-degenerate perturbation theory in second order

If we include λ with V, the states and energy levels in second order are

$$\begin{aligned}|\psi_i\rangle &= |\psi_i^{(0)}\rangle + |\psi_i^{(1)}\rangle + |\psi_i^{(2)}\rangle \\ &= |\psi_i^{(0)}\rangle + \sum\!\!\!\!\!\!\int_{j\neq i} |\psi_j^{(0)}\rangle \frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} \\ &\quad + \sum\!\!\!\!\!\!\int_{j,k\neq i} |\psi_j^{(0)}\rangle \frac{\langle\psi_j^{(0)}|V|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)\left(E_i^{(0)} - E_k^{(0)}\right)} \\ &\quad - \sum\!\!\!\!\!\!\int_{j\neq i} |\psi_j^{(0)}\rangle \frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)} - E_j^{(0)}\right)^2}\end{aligned} \tag{9.10}$$

and

$$E_i = E_i^{(0)} + \langle\psi_i^{(0)}|V|\psi_i^{(0)}\rangle + \sum\!\!\!\!\!\!\int_{j\neq i} \frac{|\langle\psi_i^{(0)}|V|\psi_j^{(0)}\rangle|^2}{E_i^{(0)} - E_j^{(0)}}. \tag{9.11}$$

The second order states $|\psi_i\rangle$ are not normalized any more,

$$\langle\psi_i|\psi_j\rangle = \delta_{ij} + \mathcal{O}(\lambda^2)\delta_{ij}.$$

Normalization is preserved in first order due to

$$\langle\psi_i^{(0)}|\psi_j^{(1)}\rangle + \langle\psi_i^{(1)}|\psi_j^{(0)}\rangle = 0,$$

but in second order we have

$$\langle\psi_i^{(0)}|\psi_j^{(2)}\rangle + \langle\psi_i^{(1)}|\psi_j^{(1)}\rangle + \langle\psi_i^{(2)}|\psi_j^{(0)}\rangle = \sum\!\!\!\!\!\!\int_{k\neq i} \frac{|\langle\psi_i^{(0)}|V|\psi_k^{(0)}\rangle|^2}{\left(E_i^{(0)} - E_k^{(0)}\right)^2}\delta_{ij}.$$

However, we can add to the leading therm $|\psi_i^{(0)}\rangle$ in $|\psi_i\rangle$ a term of the form $|\psi_i^{(0)}\rangle\mathcal{O}(\lambda^2)$ and still preserve the master equation (9.3) to second order. We

can therefore rescale (9.10) by a factor $[1+\mathcal{O}(\lambda^2)]^{-1/2}$ to a normalized second order state

$$\begin{aligned}|\psi_i\rangle = |\psi_i^{(0)}\rangle - \frac{1}{2}|\psi_i^{(0)}\rangle \sum\!\!\!\!\!\!\int_{j\neq i} \frac{|\langle\psi_i^{(0)}|V|\psi_j^{(0)}\rangle|^2}{\left(E_i^{(0)}-E_j^{(0)}\right)^2} + \sum\!\!\!\!\!\!\int_{j\neq i} |\psi_j^{(0)}\rangle \frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{E_i^{(0)}-E_j^{(0)}} \\ + \sum\!\!\!\!\!\!\int_{j,k\neq i} |\psi_j^{(0)}\rangle \frac{\langle\psi_j^{(0)}|V|\psi_k^{(0)}\rangle\langle\psi_k^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)}-E_j^{(0)}\right)\left(E_i^{(0)}-E_k^{(0)}\right)} \\ - \sum\!\!\!\!\!\!\int_{j\neq i} |\psi_j^{(0)}\rangle \frac{\langle\psi_j^{(0)}|V|\psi_i^{(0)}\rangle\langle\psi_i^{(0)}|V|\psi_i^{(0)}\rangle}{\left(E_i^{(0)}-E_j^{(0)}\right)^2}. \end{aligned} \tag{9.12}$$

Now the second order shift is not orthogonal to $|\psi_i^{(0)}\rangle$ any more, but we still have a solution of equation (9.3) to second order.

9.2 Time-independent perturbation theory with degenerate energy levels

Now we admit degeneracy of energy levels of our unperturbed Hamiltonian H_0. Time-independent perturbation theory in the previous section repeatedly involved division by energy differences $[E_i^{(0)}-E_j^{(0)}]_{i\neq j}$. This will not be possible any more for pairs of degenerate energy levels, and we have to carefully reconsider each step in the previous derivation if degeneracies are involved.
The full Hamiltonian and the 0-th order results are now

$$H = H_0 + \lambda V,\ H_0|\psi_{j\alpha}^{(0)}\rangle = E_j^{(0)}|\psi_{j\alpha}^{(0)}\rangle,$$

where Greek indices denote sets of degeneracy indices. For example, if H_0 would correspond to a hydrogen atom, the quantum number j would correspond to the principal quantum number n of a bound state or the wave number k of a spherical Coulomb wave, and the degeneracy index α would correspond to the set of angular momentum quantum number, magnetic quantum number, and spin projection, $\alpha = \{\ell, m_\ell, m_s\}$. For the same reasons as in equation (9.9), the energy level for which we wish to calculate an approximation must be discrete, i.e. in the hydrogen atom we could study perturbations of the bound states and energy levels with the techniques of this chapter, but not perturbations of Coulomb waves.
We denote the degeneracy subspace to the energy level $E_j^{(0)}$ as $\mathcal{E}_j$ and the projector on $\mathcal{E}_j$ is

$$\mathcal{P}_j^{(0)} = \sum_\alpha |\psi_{j\alpha}^{(0)}\rangle\langle\psi_{j\alpha}^{(0)}|.$$

As in the previous section, we wish to calculate approximations for the energy level $E_{i\alpha}$ and corresponding eigenstates $|\psi_{i\alpha}\rangle$, $H|\psi_{i\alpha}\rangle = E_{i\alpha}|\psi_{i\alpha}\rangle$, which arise from the energy level $E_i^{(0)}$ and the eigenstates $|\psi_{i\alpha}^{(0)}\rangle$ due to the perturbation

V. The energy level $E_i^{(0)}$ may split into several energy levels $E_{i\alpha}$ because the perturbation might lift the degeneracy of $E_i^{(0)}$. We will actually assume that the perturbation V lifts the degeneracy of the energy level $E_i^{(0)}$ already at first order, $E_{i\alpha}^{(1)} \neq E_{i\beta}^{(1)}$ if $\alpha \neq \beta$.
The Rayleigh-Ritz-Schrödinger *ansatz* is

$$|\psi_{i\alpha}\rangle = \sum_{n\geq 0} \lambda^n |\psi_{i\alpha}^{(n)}\rangle, \quad \langle \psi_{i\alpha}^{(0)} | \psi_{i\alpha}^{(n\geq 1)}\rangle = 0, \quad E_{i\alpha} = \sum_{n\geq 0} \lambda^n E_{i\alpha}^{(n)}. \tag{9.13}$$

Substitution into the full time-independent Schrödinger equation yields

$$\begin{aligned}\sum_{n\geq 0} \lambda^n H_0 |\psi_{i\alpha}^{(n)}\rangle + \sum_{n\geq 0} \lambda^{n+1} V |\psi_{i\alpha}^{(n)}\rangle &= \sum_{m,n\geq 0} \lambda^{m+n} E_{i\alpha}^{(m)} |\psi_{i\alpha}^{(n)}\rangle \\ &= \sum_{n\geq 0} \sum_{m=0}^{n} \lambda^n E_{i\alpha}^{(m)} |\psi_{i\alpha}^{(n-m)}\rangle.\end{aligned}$$

This is yields in $(n+1)$-st order for $n \geq 0$

$$H_0 |\psi_{i\alpha}^{(n+1)}\rangle + V |\psi_{i\alpha}^{(n)}\rangle = \sum_{m=0}^{n+1} E_{i\alpha}^{(m)} |\psi_{i\alpha}^{(n-m+1)}\rangle. \tag{9.14}$$

We determine the corrections $|\psi_{i\alpha}^{(n\geq 1)}\rangle$ to the wave functions through their projections $\langle \psi_{j\beta}^{(0)} | \psi_{i\alpha}^{(n\geq 1)}\rangle$ onto the basis of unperturbed states. Projection of equation (9.14) yields

$$\begin{aligned}E_j^{(0)} \langle \psi_{j\beta}^{(0)} | \psi_{i\alpha}^{(n+1)}\rangle + \langle \psi_{j\beta}^{(0)} | V | \psi_{i\alpha}^{(n)}\rangle &= \sum_{m=0}^{n} E_{i\alpha}^{(m)} \langle \psi_{j\beta}^{(0)} | \psi_{i\alpha}^{(n-m+1)}\rangle \\ &\quad + E_{i\alpha}^{(n+1)} \delta_{ij} \delta_{\alpha\beta}.\end{aligned} \tag{9.15}$$

First order corrections to the energy levels

The first order equations ($n = 0$ in equation (9.15)) yield for $j = i$ and $\beta = \alpha$ the equation

$$E_{i\alpha}^{(1)} = \langle \psi_{i\alpha}^{(0)} | V | \psi_{i\alpha}^{(0)}\rangle, \tag{9.16}$$

while $j = i$, $\alpha \neq \beta$ imposes a consistency condition on the choice of basis of unperturbed states,

$$\langle \psi_{i\beta}^{(0)} | V | \psi_{i\alpha}^{(0)}\rangle \Big|_{\beta\neq\alpha} = 0, \tag{9.17}$$

This condition means that we have to diagonalize V first *within each degeneracy subspace* $\mathcal{E}_i$ in the sense

$$V |\psi_{i\alpha}^{(0)}\rangle = E_{i\alpha}^{(1)} |\psi_{i\alpha}^{(0)}\rangle + \cancel{\sum_{j\neq i}} \sum_{\beta} |\psi_{j\beta}^{(0)}\rangle \langle \psi_{j\beta}^{(0)} | V | \psi_{i\alpha}^{(0)}\rangle, \tag{9.18}$$

before we can use the perturbation *ansatz* (9.13), and according to (9.16) the first order energy corrections $E^{(1)}_{i\alpha}$ are the corresponding eigenvalues in the i-th degeneracy subspace. If the first order energy corrections $E^{(1)}_{i\alpha}$ are all we care about, this means that we can calculate them from the eigenvalue conditions

$$\det\left[\langle\psi^{(0)}_{i\beta}|V|\psi^{(0)}_{i\alpha}\rangle - E^{(1)}_{i\alpha}\delta_{\alpha\beta}\right] = 0, \tag{9.19}$$

using any initial choice of unperturbed orthogonal energy eigenstates. But that would achieve only a very limited objective.
As also indicated in equation (9.18), diagonalization within the subspaces means only diagonalization of the operators $\mathcal{P}^{(0)}_i V \mathcal{P}^{(0)}_i$, which does *not* amount to total diagonalization of V,

$$\sum_i \mathcal{P}^{(0)}_i V \mathcal{P}^{(0)}_i \neq V = \sum_{i,j} \mathcal{P}^{(0)}_i V \mathcal{P}^{(0)}_j.$$

We still will have non-vanishing transition matrix elements $\langle\psi^{(0)}_{j\beta}|V|\psi^{(0)}_{i\alpha}\rangle \neq 0$ between different degeneracy subspaces $i \neq j$.

First order corrections to the energy eigenstates

Setting $i \neq j$ in equation (9.15) yields a part of the first order corrections to the wave functions,

$$\langle\psi^{(0)}_{j\beta}|\psi^{(1)}_{i\alpha}\rangle = \frac{\langle\psi^{(0)}_{j\beta}|V|\psi^{(0)}_{i\alpha}\rangle}{E^{(0)}_i - E^{(0)}_j}. \tag{9.20}$$

However, this yields only the projections $\langle\psi^{(0)}_{j\beta}|\psi^{(1)}_{i\alpha}\rangle$ of the first order corrections $|\psi^{(1)}_{i\alpha}\rangle$ onto the unperturbed states for $j \neq i$. We need to use $j = i$ in the second order equations to calculate the missing terms $\langle\psi^{(0)}_{i\beta}|\psi^{(1)}_{i\alpha}\rangle$, $(\beta \neq \alpha)$, for the first order corrections.
Equation (9.15) yields for $n = 1$, $j = i$ and $\beta \neq \alpha$ the equation

$$\langle\psi^{(0)}_{i\beta}|V|\psi^{(1)}_{i\alpha}\rangle\Big|_{\beta\neq\alpha} = E^{(1)}_{i\alpha}\ \langle\psi^{(0)}_{i\beta}|\psi^{(1)}_{i\alpha}\rangle\Big|_{\beta\neq\alpha}$$

and after substitution of equations (9.16, 9.17, 9.20)

$$\begin{aligned}\left(E^{(1)}_{i\alpha} - E^{(1)}_{i\beta}\right)\ \langle\psi^{(0)}_{i\beta}|\psi^{(1)}_{i\alpha}\rangle\Big|_{\beta\neq\alpha} &= \sum_{j\neq i}\sum_{\gamma}\langle\psi^{(0)}_{i\beta}|V|\psi^{(0)}_{j\gamma}\rangle\langle\psi^{(0)}_{j\gamma}|\psi^{(1)}_{i\alpha}\rangle \\ &= \sum_{j\neq i}\sum_{\gamma}\frac{\langle\psi^{(0)}_{i\beta}|V|\psi^{(0)}_{j\gamma}\rangle\langle\psi^{(0)}_{j\gamma}|V|\psi^{(0)}_{i\alpha}\rangle}{E^{(0)}_i - E^{(0)}_j},\end{aligned}$$

i.e. we find the missing pieces of the first order corrections to the states

$$\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle\Big|_{\beta\neq\alpha} = \frac{1}{\langle\psi_{i\alpha}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle - \langle\psi_{i\beta}^{(0)}|V|\psi_{i\beta}^{(0)}\rangle} \times \sum\!\!\!\!\!\!\int_{j\neq i} \sum_{\gamma} \frac{\langle\psi_{i\beta}^{(0)}|V|\psi_{j\gamma}^{(0)}\rangle\langle\psi_{j\gamma}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle}{E_i^{(0)} - E_j^{(0)}} \tag{9.21}$$

if V has removed the degeneracy between $|\psi_{i\alpha}\rangle$ and $|\psi_{i\beta}\rangle$ in first order, $E_{i\alpha}^{(1)} \neq E_{i\beta}^{(1)}$.

Recursive solution of equation (9.15) for $n \geq 1$

We first rewrite equation (9.15) by inserting

$$1 = \sum\!\!\!\!\!\!\int_{k,\gamma} |\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|$$

in the matrix element of V, and using equations (9.16, 9.17):

$$E_j^{(0)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n+1)}\rangle + E_{j\beta}^{(1)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n)}\rangle + \sum\!\!\!\!\!\!\int_{k\neq j} \sum_{\gamma} \langle\psi_{j\beta}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(n)}\rangle$$

$$= E_i^{(0)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n+1)}\rangle + E_{i\alpha}^{(1)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n)}\rangle + \Theta(n \geq 2)\sum_{m=2}^{n} E_{i\alpha}^{(m)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n-m+1)}\rangle + E_{i\alpha}^{(n+1)}\delta_{ij}\delta_{\alpha\beta}. \tag{9.22}$$

Substitution of $j = i$ and $\beta = \alpha$ yields

$$E_{i\alpha}^{(n+1)} = \sum\!\!\!\!\!\!\int_{k\neq i} \sum_{\gamma} \langle\psi_{i\alpha}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(n)}\rangle, \tag{9.23}$$

where equations (9.13, 9.17) have been used. The second order correction is in particular with equation (9.20):

$$E_{i\alpha}^{(2)} = \sum\!\!\!\!\!\!\int_{j\neq i} \sum_{\beta} \frac{|\langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle|^2}{E_i^{(0)} - E_j^{(0)}}. \tag{9.24}$$

We find again that the second order correction to the ground state energy is always negative.

For the higher order shifts of the states we find for $j \neq i$ in equation (9.22)

$$\left(E_i^{(0)} - E_j^{(0)}\right)\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n+1)}\rangle = \langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(n)}\rangle - \sum_{m=1}^{n} E_{i\alpha}^{(m)}\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n-m+1)}\rangle$$

$$= \langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(n)}\rangle - \langle\psi_{i\alpha}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n)}\rangle - \Theta(n \geq 2)\sum_{m=1}^{n-1} \sum\!\!\!\!\!\!\int_{k\neq i} \sum_{\gamma} \langle\psi_{i\alpha}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle \times \langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(m)}\rangle\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n-m)}\rangle,$$

which gives us the contributions $\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(n+1)}\rangle\Big|_{j\neq i}$ to the $(n+1)$-st order wave function corrections.
Substitution of $i=j$, $\alpha\neq\beta$ yields finally

$$\begin{aligned}\left(E_{i\alpha}^{(1)}-E_{i\beta}^{(1)}\right)\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(n\geq 1)}\rangle\Big|_{\beta\neq\alpha} &= \sum\!\!\!\!\!\!\int_{k\neq i}\sum_{\gamma}\langle\psi_{i\beta}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(n)}\rangle \\ &\quad -\Theta(n\geq 2)\sum_{m=2}^{n}E_{i\alpha}^{(m)}\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(n-m+1)}\rangle \\ &= \sum\!\!\!\!\!\!\int_{k\neq i}\sum_{\gamma}\langle\psi_{i\beta}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(n)}\rangle \\ &\quad -\Theta(n\geq 2)\sum_{m=1}^{n-1}\sum\!\!\!\!\!\!\int_{k\neq i}\sum_{\gamma}\langle\psi_{i\alpha}^{(0)}|V|\psi_{k\gamma}^{(0)}\rangle \\ &\quad \times\langle\psi_{k\gamma}^{(0)}|\psi_{i\alpha}^{(m)}\rangle\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(n-m)}\rangle.\end{aligned}$$

This gives us the missing pieces $\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(n)}\rangle\Big|_{\beta\neq\alpha}$ of the n-th order wave function correction for $E_{i\alpha}^{(1)}\neq E_{i\beta}^{(1)}$.

Summary of first order perturbations of the level $E_i^{(0)}$ if the perturbation lifts the degeneracy of the level in first order

We must diagonalize the perturbation operator V within the degeneracy subspace $\mathcal{E}_i$ in the sense of (9.18), i.e. we must choose the unperturbed eigenstates $|\psi_{i\alpha}^{(0)}\rangle$ such that the equation

$$\langle\psi_{i\alpha}^{(0)}|V|\psi_{i\beta}^{(0)}\rangle=E_{i\alpha}^{(1)}\delta_{\alpha\beta}$$

also holds for $\alpha\neq\beta$.
The first order shifts of the energy eigenstates are

$$\langle\psi_{j\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle\Big|_{j\neq i}=\frac{\langle\psi_{j\beta}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle}{E_i^{(0)}-E_j^{(0)}},$$

$$\begin{aligned}\langle\psi_{i\beta}^{(0)}|\psi_{i\alpha}^{(1)}\rangle\Big|_{\beta\neq\alpha} &= \frac{1}{\langle\psi_{i\alpha}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle-\langle\psi_{i\beta}^{(0)}|V|\psi_{i\beta}^{(0)}\rangle} \\ &\quad\times\sum\!\!\!\!\!\!\int_{j\neq i}\sum_{\gamma}\frac{\langle\psi_{i\beta}^{(0)}|V|\psi_{j\gamma}^{(0)}\rangle\langle\psi_{j\gamma}^{(0)}|V|\psi_{i\alpha}^{(0)}\rangle}{E_i^{(0)}-E_j^{(0)}}.\end{aligned}$$

The last equation requires that the first order shifts have completely removed the degeneracies in the i-th energy level, $E_{i\beta}^{(1)}\neq E_{i\alpha}^{(1)}$ for $\beta\neq\alpha$.

9.3 Problems

9.1 A one-dimensional harmonic oscillator is perturbed by a term $V = \lambda[(a^+)^2 + a^2]^2$. Calculate the first and second order corrections to the ground state energy and wave function.

9.2 An atom on a surface is prevented from moving along the surface through a two-dimensional potential

$$V(x,y) = \frac{1}{2}m\omega^2(x^2+y^2) + Ax^4 + By^4, \quad A \geq 0, \quad B \geq 0.$$

Find an approximation H_0 for the Hamiltonian of the atom where you can write down exact energy levels and eigenstates for the atom.
Use the remaining terms in $H - H_0$ to calculate first order corrections to the energy levels and eigenstates of the atom.

9.3 Which results do you get for the perturbed system from 9.2 in second order perturbation theory?

9.4 Suppose that the perturbation V has removed all degeneracies in all energy levels of an unperturbed system. Show that all the first order states $|\psi_{i\alpha}^{(0)}\rangle + |\psi_{i\alpha}^{(1)}\rangle$ are orthonormal in first order.

9.5 A hydrogen atom is perturbed by a static electric field $\boldsymbol{E} = \mathcal{E}\boldsymbol{e}_z$ in z direction. This field induces an extra potential $V = -e\Phi = e\mathcal{E}z$ in the Hamiltonian for relative motion.
9.5a Calculate the shift of the ground state energy up to second order in $\mathcal{E}$.
9.5b Calculate the shift of the ground state wave function up to second order in $\mathcal{E}$.
9.5c Which constraints on $\mathcal{E}$ do you find from the requirement of applicability of perturbation theory?

9.6 Perform the tasks from problem 18.4 for the 2s state $|2,0,0\rangle$ of hydrogen.

9.7 A two-level system has two energy eigenstates $|E_\pm\rangle$ with energies

$$H_0|E_\pm\rangle = \left(E_0 \pm \frac{\Delta E}{2}\right)|E_\pm\rangle, \quad \Delta E \neq 0.$$

We can use 2-spinor notation such that a general state in the two-level system is

$$|\psi\rangle = \sum_\pm |E_\pm\rangle\langle E_\pm|\psi\rangle \to \psi = \begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}, \quad \psi_1 = \langle E_+|\psi\rangle, \quad \psi_2 = \langle E_-|\psi\rangle.$$

The Hamiltonian in 2-spinor notation is

$$H_0 = E_0\underline{1} + \frac{\Delta E}{2}\underline{\sigma}_3.$$

We now perturb the Hamiltonian $H_0 \to H = H_0 + V$ through a term

$$V = \frac{V_1}{2}\underline{\sigma}_1 + \frac{V_2}{2}\underline{\sigma}_2.$$

9.7a Calculate the first order corrections to the energy levels and eigenstates due to the perturbation V.
9.7b Calculate the second order corrections to the energy levels and eigenstates due to the perturbation V.
9.7c The Hamiltonian H is a hermitian 2×2 matrix which can be diagonalized exactly.
Calculate the exact energy levels and eigenstates of H. Compare with the perturbative results from 9.7a and 9.7b.

Chapter 10

Quantum Aspects of Materials I

Quantum mechanics is indispensable for the understanding of materials. Solid state physics, in return, provides beautiful illustrations for the impact of quantum dynamics on allowed energy levels in a system, for wave-particle duality, and for applications of perturbation theory.

In the present chapter we will focus on Bloch's theorem, the duality between Bloch and Wannier states, the emergence of energy bands in crystals, and the emergence of effective mass in kp perturbation theory. We will do this for one-dimensional lattices, since this captures the essential ideas. Students who would like to follow up on our introductory exposition and understand the profound impact of quantum mechanics on every physical property of materials at a deeper level should consult the monographs of Callaway [4], Ibach and Lüth [15], Kittel [20] or Madelung [23], or any of the other excellent texts on condensed matter physics - and they should include courses on condensed matter physics in their curriculum!

10.1 Bloch's theorem

Electrons in solid materials provide a particularly beautiful realization of wave-particle duality. Bloch's theorem covers the wave aspects of this duality. From a practical perspective, Bloch's theorem implies that we can discuss electrons in terms of states which sample the whole lattice of ion cores in a solid material. This has important implications for the energy levels of electrons in materials, and therefore for all physical properties of materials.

It is useful to recall the theory of discrete Fourier transforms as a preparation for the proof of Bloch's theorem. We write the discrete Fourier expansion for functions $f(x)$ with periodicity a as

$$f(x) = \sum_{n=-\infty}^{\infty} f_n \exp\Big(2\pi \mathrm{i} \frac{nx}{a}\Big). \tag{10.1}$$

R. Dick, *Advanced Quantum Mechanics: Materials and Photons*,
Graduate Texts in Physics, DOI 10.1007/978-1-4419-8077-9_10,
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The orthogonality relation

$$\frac{1}{a}\int_0^a dx\, \exp\Big(2\pi\mathrm{i}\frac{mx}{a}\Big)\exp\Big(-2\pi\mathrm{i}\frac{nx}{a}\Big) = \delta_{mn} \tag{10.2}$$

yields the inversion

$$f_n = \frac{1}{a}\int_0^a dx\, f(x)\exp\Big(-2\pi\mathrm{i}\frac{nx}{a}\Big),$$

and substituting this back into equation (10.1) yields a representation of the δ-function in a finite interval of length a,

$$\frac{1}{a}\sum_{n=-\infty}^{\infty}\exp\left(2\pi\mathrm{i}n\frac{x-x'}{a}\right) = \delta(x-x'), \tag{10.3}$$

or equivalently

$$\sum_{n=-\infty}^{\infty}\exp(\mathrm{i}n\xi) = 2\pi\delta(\xi). \tag{10.4}$$

Equation (10.3) is the completeness relation for the Fourier monomials on an interval of length a.
The Hamiltonian for electrons in a lattice with periodicity a is

$$H = \frac{\mathrm{p}^2}{2m} + V(\mathrm{x}),$$

where the potential operator has the periodicity of the lattice,

$$V(\mathrm{x}) = V(\mathrm{x}+a) = \exp\left(\frac{\mathrm{i}}{\hbar}a\mathrm{p}\right)V(\mathrm{x})\exp\left(-\frac{\mathrm{i}}{\hbar}a\mathrm{p}\right).$$

This implies

$$\exp\left(\frac{\mathrm{i}}{\hbar}a\mathrm{p}\right)H = H\exp\left(\frac{\mathrm{i}}{\hbar}a\mathrm{p}\right),$$

and therefore eigenspaces of H decay into eigenspaces of the lattice translation operator

$$T(a) = \exp\left(\frac{\mathrm{i}}{\hbar}a\mathrm{p}\right).$$

The eigenvalues of this unitary operator must be pure phase factors[1],

$$\exp\left(\frac{\mathrm{i}}{\hbar}a\mathrm{p}\right)|E_n,k\rangle = \exp(\mathrm{i}ka)\,|E_n,k\rangle.$$

[1]This is a consequence of Schur's Lemma in group theory: Abelian symmetry groups have one-dimensional irreducible representations.

Let us repeat this result in the x-representation:

$$\langle x|\exp\left(\frac{\mathrm{i}}{\hbar}ap\right)|E_n,k\rangle = \exp\left(a\frac{d}{dx}\right)\langle x|E_n,k\rangle = \langle x+a|E_n,k\rangle$$
$$= \exp(\mathrm{i}ka)\,\langle x|E_n,k\rangle.$$

This means that the energy eigenstate $\langle x|E_n,k\rangle \equiv \psi_n(k,x)$ has exactly the same periodicity properties under lattice translations as the plane wave $\langle x|k\rangle = \exp(\mathrm{i}kx)/\sqrt{2\pi}$. The ratio $\psi_n(k,x)/\langle x|k\rangle$ must therefore be a periodic function! This is Bloch's theorem in solid state physics[2]:
Energy eigenstates in a periodic lattice can always be written as the product of a periodic function $u_n(k,x+a) = u_n(k,x)$ with a plane wave,

$$\psi_n(k,x) = \sqrt{\frac{a}{2\pi}}\exp(\mathrm{i}kx)u_n(k,x). \tag{10.5}$$

The quasi-periodicity parameter k has momentum like properties, but is not the momentum $\langle E_n,k|p|E_n,k\rangle$ in the state $|E_n,k\rangle$. Therefore it is often denoted as a quasi-momentum or a pseudomomentum.
Periodicity of the modulation factor $u_n(k,x)$ implies the expansions

$$u_n(k,x) = \sum_{\ell\in\mathbb{Z}} u_{n;\ell}(k)\exp\left(2\pi\mathrm{i}\frac{\ell x}{a}\right),$$

$$u_{n;\ell}(k) = \frac{1}{a}\int_0^a dx\, u_n(k,x)\exp\left(-2\pi\mathrm{i}\frac{\ell x}{a}\right).$$

We denote the eigenfunctions $\psi_n(k,x) \equiv \langle x|E_n,k\rangle$ of the lattice Hamiltonian as *Bloch functions*. The corresponding periodic functions $u_n(k,x) \equiv \langle x|E_n(k)\rangle$ will be denoted as *Bloch factors*.
For arbitrary $\ell \in \mathbb{Z}$ the eigenvalues of the lattice translations satisfy

$$\exp(\mathrm{i}ka) = \exp\left[\mathrm{i}\left(k+\frac{2\pi\ell}{a}\right)a\right],$$

and therefore the quasi-momentum k can be restricted to the region

$$-\frac{\pi}{a} < k \le \frac{\pi}{a}, \tag{10.6}$$

which is denoted as the first Brillouin zone of the (rescaled) dual lattice.
The index n apparently enumerates different energy levels for each value of k in the first Brillouin zone. The functions $E_n(k)$ are known as energy bands, and we will see below that there are indeed enumerably many energy bands in a lattice.

[2] F. Bloch, Z. Phys. 52, 555 (1929). As a mathematical theorem in the theory of differential equations it is known as Floquet's theorem due to G. Floquet, Ann. sci. de l'É.N.S., 2e série, 12, 47 (1883).

Orthogonality of the periodic Bloch factors

The orthogonality relation for the energy eigenstates $\psi_n(k,x) = \langle x|E_n,k\rangle$ implies an orthogonality property for the periodic Bloch factors $u_n(k,x) = \langle x|E_n(k)\rangle$. We have

$$\begin{aligned}\delta_{mn}\delta(k-k') &= \langle E_m,k'|E_n,k\rangle \\ &= \frac{a}{2\pi}\int_{-\infty}^{\infty} dx\, \exp[\mathrm{i}(k-k')x]\, u_m^+(k',x)u_n(k,x) \\ &= \frac{a}{2\pi}\sum_{\ell\in\mathbb{Z}} \exp[\mathrm{i}(k-k')\ell a] \\ &\quad \times \int_0^a dx\, \exp[\mathrm{i}(k-k')x]\, u_m^+(k',x)u_n(k,x). \end{aligned} \tag{10.7}$$

Equation (10.4) implies

$$\sum_{\ell\in\mathbb{Z}} \exp[\mathrm{i}(k-k')\ell a] = \frac{2\pi}{a}\delta(k-k'), \tag{10.8}$$

and substitution of this into equation (10.7) yields the orthogonality relations for the periodic Bloch factors,

$$\int_0^a dx\, u_m^+(k,x)u_n(k,x) = a\sum_\ell u_{m;\ell}^+(k)u_{n;\ell}(k) = \delta_{mn}. \tag{10.9}$$

Note that this in turn also implies a normalization of the Bloch functions in the lattice cell,

$$\int_0^a dx\, |\psi_n(k,x)|^2 = \frac{a}{2\pi}.$$

The plane wave normalization in (10.7) implies length dimension 0 for the Bloch functions and length dimension -1/2 for the Bloch factors.
We remark that the completeness of the energy eigenstates yields

$$\begin{aligned}\delta(x-x') &= \sum_n \int_{-\pi/a}^{\pi/a} dk\, \langle x|E_n,k\rangle\langle E_n,k|x'\rangle \\ &= \frac{a}{2\pi}\sum_n \int_{-\pi/a}^{\pi/a} dk\, \exp[\mathrm{i}k(x-x')]\, u_n^+(k,x')u_n(k,x), \end{aligned} \tag{10.10}$$

but we cannot read off a separate relation for the Bloch factors from this.

10.2 Wannier states

The Bloch functions $\psi_n(k,x)$ are plane waves with a periodic modulation factor $u_n(k,x) = u_n(k,x+a)$, and therefore extend over the full lattice in x-space. However, due to

$$\exp(\mathrm{i}\,[k + (2\pi\ell/a)]\, a) = \exp(\mathrm{i}ka)$$

the quasi-periodicity parameter k was restricted to the first Brillouin zone

$$-\frac{\pi}{a} < k \leq \frac{\pi}{a}, \tag{10.11}$$

i.e. as a function of k, $\psi_n(k,x)$ is only defined in the finite interval (10.11) (or equivalently has periodicity under shifts of k by multiples of $2\pi/a$). This implies the expansions[3]

$$\psi_n(k,x) = \sqrt{\frac{a}{2\pi}}\exp(\mathrm{i}kx)u_n(k,x) = \sqrt{\frac{a}{2\pi}}\sum_{\nu\in\mathbb{Z}} w_{n,\nu}(x)\exp(\mathrm{i}\nu ka), \tag{10.12}$$

$$u_n(k,x) = \sum_{\nu\in\mathbb{Z}} w_{n,\nu}(x)\exp[-\mathrm{i}k(x-\nu a)]. \tag{10.13}$$

The states $w_{n,\nu}(x)$ are apparently Fourier transforms of the Bloch functions $\psi_n(k,x)$ with respect to the quasi-periodicity parameter k. These states are known as Wannier states.

The inversion of the expansion is

$$\begin{aligned} w_{n,\nu}(x) &= \sqrt{\frac{a}{2\pi}}\int_{-\pi/a}^{\pi/a} dk\,\psi_n(k,x)\exp(-\mathrm{i}\nu ka) \\ &= \frac{a}{2\pi}\int_{-\pi/a}^{\pi/a} dk\,u_n(k,x)\exp[\mathrm{i}k(x-\nu a)]. \end{aligned} \tag{10.14}$$

However, the periodicity $u_n(k,x-\mu a) = u_n(k,x)$ of the Bloch functions then also yields

$$w_{n,\nu}(x-\mu a) = w_{n,\nu+\mu}(x). \tag{10.15}$$

This implies in particular a localization property of Wannier states,

$$w_{n,\nu}(x) = w_{n,0}(x-\nu a). \tag{10.16}$$

Determining all the functions $w_{n,\nu}(x)$ in one cell of the direct lattice is equivalent to finding the function $w_{n,0}(x)$ over the full lattice. Furthermore, $w_{n,\nu}(x)$ depends only on $x-\nu a$, i.e. it is attached to a lattice cell[4].

Wannier states satisfy completeness relations as a consequence of the completeness relations of the Bloch states. The relations are

$$\begin{aligned} \int_{-\infty}^{\infty} dx\,w^+_{m,\mu}(x)w_{n,\nu}(x) &= \frac{a}{2\pi}\int_{-\pi/a}^{\pi/a} dk'\int_{-\pi/a}^{\pi/a} dk\int_{-\infty}^{\infty} dx\,\psi^+_m(k',x)\psi_n(k,x) \\ &\quad\times\exp[\mathrm{i}(\mu k'-\nu k)a] \\ &= \delta_{mn}\frac{a}{2\pi}\int_{-\pi/a}^{\pi/a} dk\,\exp[\mathrm{i}(\mu-\nu)ka] = \delta_{mn}\delta_{\mu\nu}, \end{aligned}$$

[3] This is exactly as in (10.1), only with periodicity $2\pi/a$.

[4] It is tempting to conclude that the Wannier functions $w_{n,\nu}(x)$ should be centered around the lattice site $x=\nu a$, but this is not what generically happens. The Wannier function $w_{n,\nu}(x)$ is usually large in a unit cell containing the lattice site $x=\nu a$, but localization around the lattice site requires inclusion of extra phase factors $\exp[\mathrm{i}\varphi(n,k)]$ in the Bloch functions, see W. Kohn, Phys. Rev. 115, 809 (1959) and F.B. Pedersen, G.T. Einevoll, P.C. Hemmer, Phys. Rev. B 44, 5470 (1991).

and

$$\sum_{n,\nu} w_{n,\nu}(x) w^+_{n,\nu}(x') = \int_{-\pi/a}^{\pi/a} dk \int_{-\pi/a}^{\pi/a} dk' \frac{a}{2\pi} \sum_{\nu} \exp[-\mathrm{i}\nu(k-k')a] \times \sum_n \psi_n(k,x)\psi^+_n(k',x') = \int_{-\pi/a}^{\pi/a} dk \int_{-\pi/a}^{\pi/a} dk'\, \delta(k-k') \sum_n \psi_n(k,x)\psi^+_n(k',x') = \int_{-\pi/a}^{\pi/a} dk \sum_n \psi_n(k,x)\psi^+_n(k,x') = \delta(x-x'). \quad (10.17)$$

The periodicity of the Bloch functions in the dual lattice

$$\psi_n(k,x) = \psi_n\left(k + \frac{2\pi}{a}, x\right)$$

implies for the Bloch factors the quasi-periodicity

$$u_n\left(k + \frac{2\pi}{a}, x\right) = \exp\left(-2\pi\mathrm{i}\frac{x}{a}\right) u_n(k,x), \quad u_{n,\ell}\left(k + \frac{2\pi}{a}\right) = u_{n,\ell+1}(k),$$

and in particular

$$u_{n,\ell}(k) = u_{n,0}\left(k + \frac{2\pi\ell}{a}\right). \quad (10.18)$$

This property of the Fourier coefficients of the Bloch factors in the dual lattice is dual to the property (10.16) of the Wannier functions in the direct lattice. Knowing all the Fourier coefficients $u_{n,\ell}(k)$ of the Bloch factors in a Brillouin zone is equivalent to knowing the Fourier coefficients $u_{n,0}(k)$ throughout the dual lattice. We can think of the functions $u_{n,-\ell}(k)$ as dual Wannier functions in k space. Indeed, these functions are related through Fourier transforms,

$$w_{n,0}(x) = \frac{a}{2\pi} \int_{-\infty}^{\infty} dk\, u_{n,0}(k) \exp(\mathrm{i}kx),$$

$$u_{n,0}(k) = \frac{1}{a} \int_{-\infty}^{\infty} dx\, w_{n,0}(x) \exp(-\mathrm{i}kx), \quad (10.19)$$

see problem 2. Knowing any particular Wannier function $w_{n,\nu}(x)$ in the whole lattice, or any particular dual Wannier function $u_{n,\ell}(k)$ everywhere in the dual lattice completely determines the Wannier and Bloch functions, and the Wannier and Bloch states for given band index n.

We can summarize the periodicity properties of the Bloch functions and the Bloch factors in the assertions that the Bloch function

$$\begin{aligned}\psi_n(k,x) &= \sqrt{\frac{a}{2\pi}}\exp(\mathrm{i}kx)u_n(k,x)\\ &= \sqrt{\frac{a}{2\pi}}\sum_{\ell\in\mathbb{Z}} u_{n,0}\left(k+\frac{2\pi\ell}{a}\right)\exp\left[\mathrm{i}\left(k+\frac{2\pi\ell}{a}\right)x\right]\\ &= \sqrt{\frac{a}{2\pi}}\sum_{\nu\in\mathbb{Z}} w_{n,0}(x+\nu a)\exp(-\mathrm{i}\nu ka) \qquad (10.20)\end{aligned}$$

is periodic in dual space and quasi-periodic in direct space, whereas the Bloch factor

$$\begin{aligned}u_n(k,x) &= \sum_{\ell\in\mathbb{Z}} u_{n,0}\left(k+\frac{2\pi\ell}{a}\right)\exp\left(2\pi\mathrm{i}\frac{\ell x}{a}\right)\\ &= \sum_{\nu\in\mathbb{Z}} w_{n,0}(x+\nu a)\exp[-\mathrm{i}k(x+\nu a)] \qquad (10.21)\end{aligned}$$

is quasi-periodic in dual space and periodic in direct space.

10.3 Time-dependent Wannier states

The usual stationary Wannier states (10.14) do not satisfy the time-independent Schrödinger equation in the crystal because they are linear combinations of stationary solutions for different eigenvalues $E_n(k)$. However, the solutions

$$\psi_n(k,x,t) = \psi_n(k,x)\exp(-\mathrm{i}E_n(k)t/\hbar)$$

of the time-dependent Schrödinger equation satisfy the same periodicity properties in the dual lattice as $\psi_n(k,x)$ because the energy bands $E_n(k)$ are periodic in the dual lattice. Therefore we can write down expansions

$$\psi_n(k,x,t) = \sqrt{\frac{a}{2\pi}}\sum_{\nu\in\mathbb{Z}} w_{n,\nu}(x,t)\exp(\mathrm{i}\nu ka), \qquad (10.22)$$

$$\begin{aligned}w_{n,\nu}(x,t) &= \sqrt{\frac{a}{2\pi}}\int_{-\pi/a}^{\pi/a} dk\,\psi_n(k,x,t)\exp(-\mathrm{i}\nu ka)\\ &= \frac{a}{2\pi}\int_{-\pi/a}^{\pi/a} dk\,u_n(k,x)\exp[\mathrm{i}k(x-\nu a)]\exp\left(-\frac{\mathrm{i}}{\hbar}E_n(k)t\right). \qquad (10.23)\end{aligned}$$

The time-dependent Wannier states (10.23) also satisfy completeness relations,

$$\int_{-\infty}^{\infty} dx\, w^+_{m,\mu}(x,t)w_{n,\nu}(x,t) = \delta_{mn}\delta_{\mu\nu} \qquad (10.24)$$

and

$$\sum_{n,\nu} w_{n,\nu}(x,t)w^+_{n,\nu}(x',t) = \delta(x-x'), \qquad (10.25)$$

and the periodicity $u_n(k, x-\mu a) = u_n(k, x)$ of the Bloch functions also implies localization of the time-dependent states,

$$w_{n,\nu}(x,t) = w_{n,0}(x-\nu a, t). \tag{10.26}$$

These states are therefore still associated with individual lattice sites, but contrary to the states (10.14), the states (10.23) are solutions of a Schrödinger equation in the lattice,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}w_{n,\nu}(x,t) = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right) w_{n,\nu}(x,t).$$

We can think of this as a manifestation of wave-particle duality for electrons in a crystal. We can describe electrons as waves penetrating the whole crystal, or as particles associated with particular lattice sites[5].

10.4 The Kronig-Penney model

The Kronig-Penney model[6] discusses motion of non-relativistic particles in a periodic piecewise constant potential. It provides a beautiful explanation for the emergence of energy bands in materials by demonstrating that only certain energy ranges in a periodic potential can yield electron states which comply with Bloch's theorem. We discuss the simplified version where the periodic potential is a series of δ-peaks at distance a,

$$V(x) = V_0 b\sum_{\nu\in\mathbb{Z}}\delta(x-\nu a). \tag{10.27}$$

V_0 is a constant energy, while $b > 0$ is a constant length to make the equation dimensionally correct. In a model with finite width, V_0 would be the height of a barrier and b the width.
Since we have vanishing potential for $-a < x < 0$, the energy eigenstates

$$\langle x|E,k\rangle = \sqrt{\frac{a}{2\pi}}\exp(\mathrm{i}kx)u(k,x)$$

in this region must satisfy

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\langle x|E,k\rangle = E\langle x|E,k\rangle, \quad -a < x < 0,$$

i.e. they must be combinations of plane waves $\exp(\pm\mathrm{i}Kx)$ with wave vector $K = \sqrt{2mE}/\hbar$ for $E > 0$, or combinations of real exponentials $\exp(\pm Kx)$ with $K = \sqrt{-2mE}/\hbar$ for $E < 0$. Solution with positive energy exist both for $V_0 > 0$ and $V_0 < 0$, but negative energy solutions exist only for $V_0 < 0$.

[5] However, the function $|w_{n,\nu}(x,t)|$ for higher n can have its maxima far from the lattice site νa.

[6] R. de L. Kronig & W.G. Penney, Proc. Roy. Soc. London A 130, 449 (1931).

We discuss the positive energy solutions first. Once we know the energy eigenstates in one interval of length a, we know them everywhere, because we know from Bloch's theorem that whenever we proceed by a length a the wave function only changes by a factor $\exp(\mathrm{i}ka)$. For the intervals $-a < x < 0$ and $0 < x < a$ this implies in particular (with $E > 0$)

$$\langle x|E,k\rangle = \begin{cases} A\exp[\mathrm{i}Kx] + B\exp[-\mathrm{i}Kx], & -a \le x \le 0, \\ A\exp[\mathrm{i}(Kx - Ka + ka)] + B\exp[\mathrm{i}(Ka - Kx + ka)], \\ \quad 0 \le x \le a, \end{cases}$$

and for $(\nu-1)a < x < \nu a$:

$$\langle x|E,k\rangle = A\exp[\mathrm{i}(Kx - \nu Ka + \nu ka)] + B\exp[\mathrm{i}(\nu Ka - Kx + \nu ka)].$$

The junction conditions following from the full Schrödinger equation

$$\frac{d^2}{dx^2}\langle x|E,k\rangle + \frac{2mE}{\hbar^2}\langle x|E,k\rangle = \frac{2m}{\hbar^2}V_0 b\sum_{\nu\in\mathbb{Z}}\delta(x-\nu a)\langle x|E,k\rangle$$

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$$\lim_{\epsilon\to 0}\left(\langle \nu a+\epsilon|E,k\rangle - \langle \nu a-\epsilon|E,k\rangle\right) = 0,$$

$$\lim_{\epsilon\to+0}\left(\frac{d}{dx}\langle x|E,k\rangle\Big|_{x=\nu a+\epsilon} - \frac{d}{dx}\langle x|E,k\rangle\Big|_{x=\nu a-\epsilon}\right) = 2\frac{u}{a}\langle \nu a|E,k\rangle,$$

where the new constant $u = mV_0ab/\hbar^2$ was introduced for convenience. The resulting junction conditions are identical at all lattice points $x = \nu a$,

$$A\exp[\mathrm{i}(k-K)a] + B\exp[\mathrm{i}(k+K)a] = A+B, \tag{10.28}$$

$$\mathrm{i}KA\Big(\exp[\mathrm{i}(k-K)a]-1\Big) - \mathrm{i}KB\Big(\exp[\mathrm{i}(k+K)a]-1\Big) = 2\frac{u}{a}(A+B). \tag{10.29}$$

The requirement for existence of a non-trivial solution of these equations yields the condition

$$\begin{vmatrix} \exp[\mathrm{i}(k-K)a]-1 & \exp[\mathrm{i}(k+K)a]-1 \\ \mathrm{i}K(\exp[\mathrm{i}(k-K)a]-1) - (2u/a) & -\mathrm{i}K(\exp[\mathrm{i}(k+K)a]-1) - (2u/a) \end{vmatrix} = 0,$$

i.e.

$$\cos(Ka) + \frac{u}{Ka}\sin(Ka) = \cos(ka), \tag{10.30}$$

which in turn implies a condition for the allowed energy values $E = \hbar^2K^2/2m$,

$$\left|\cos(Ka) + \frac{u}{Ka}\sin(Ka)\right| \le 1. \tag{10.31}$$

The limit $E \to 0+$ is allowed if and only if $|1+u| \leq 1$, or equivalently if and only if $-2 \leq u \leq 0$.
The function on the left hand side of equation (10.30) is plotted for $u = 5$ in Figure 10.1 and for negative values of u in Figures 10.6 and 10.8 below. For $0 > u > -2$ the lowest energy band has both positive and negative energy values.
Negative energy solutions $E < 0$ might exist for $V_0 < 0$. The Schrödinger equation for $-a < x < 0$ and the Bloch theorem imply

$$\langle x|E,k\rangle = \begin{cases} A\exp[Kx] + B\exp[-Kx], & -a \leq x \leq 0, \\ A\exp[Kx - Ka + \mathrm{i}ka] + B\exp[Ka - Kx + \mathrm{i}ka], & \\ \quad 0 \leq x \leq a, & \end{cases}$$

with $K = \sqrt{-2mE}/\hbar$.
The matching conditions at $x = 0$ (and for any $x = \nu a$) are

$$A\exp[(\mathrm{i}k - K)a] + B\exp[(\mathrm{i}k + K)a] = A + B,$$

$$KA(\exp[(\mathrm{i}k - K)a] - 1) - KB(\exp[(\mathrm{i}k + K)a] - 1) = -\frac{2m}{\hbar^2}|V_0|b(A + B),$$

and the condition for existence of non-trivial solutions is with $u = mV_0 a\, b/\hbar^2 < 0$,

$$\begin{vmatrix} \exp[(\mathrm{i}k - K)a] - 1 & \exp[(\mathrm{i}k + K)a] - 1 \\ K(\exp[(\mathrm{i}k - K)a] - 1) - (2u/a) & -K(\exp[(\mathrm{i}k + K)a] - 1) - (2u/a) \end{vmatrix} = 0.$$

This yields

$$\cosh(Ka) + \frac{u}{Ka}\sinh(Ka) = \cos(ka) \tag{10.32}$$

The limit $E \to 0-$ exists if and only if $-2 \leq u \leq 0$, i.e. in the same range for V_0 which was found for $E \to 0+$.
For $V_0 < 0$ one always finds one negative energy band (besides the positive energy bands), see e.g. Figures 10.5 and 10.7. This negative energy band goes from a minimum at $k = 0$ to positive maxima at $k = \pm\pi/a$ if $-2 \leq u \leq 0$, by joining to a positive energy branch at some intermediate values $\pm k_0$. The intermediate value k_0 with $E(k_0) = 0$ satisfies

$$\cos(k_0 a) = 1 + u.$$

For $u < -2$ the lowest band is entirely in the negative energy range, but still with the minimum at $k = 0$ and the maxima at $k = \pm\pi/a$.
It is useful to plot the functions $f(Ka) = \cos(Ka) + (u/Ka)\sin(Ka)$, and for negative u also $g(Ka) = \cosh(Ka) + (u/Ka)\sinh(Ka)$ to analyze the implications of the conditions (10.30) and (10.32). We will do this for $u = 5$.

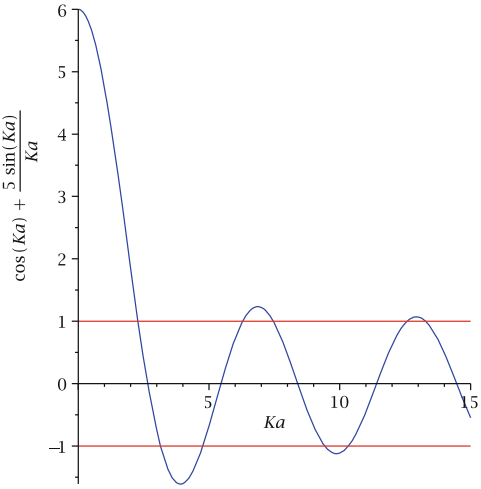


Figure 10.1: The function $f(Ka) = \cos(Ka) + (u/Ka)\sin(Ka)$ for $u = 5$.

Increasing Ka in Figure 10.1 corresponds to increasing energy $E = \hbar^2 K^2/2m$. Due to the condition (10.30) there are no allowed energies for $0 \leq Ka < K_1 a \simeq 2.284$ where $f(Ka) > 1$. At $K_1 a$ we have the lowest allowed energy value $\hbar^2 K_1^2/2m$ with corresponding pseudomomentum $ka = 0$. Between $K_1 a \leq Ka \leq K_2 a = \pi$ the energy increases to $\hbar^2\pi^2/2ma^2$ and the values of $|ka|$ increase to the boundaries $|ka| = \pi$ of the Brillouin zone. The width of this lowest energy band is

$$W = \frac{\hbar^2}{2m}\left(K_2^2 - K_1^2\right) \simeq \frac{\hbar^2}{2ma^2}\left(\pi^2 - 2.284^2\right).$$

For $\pi < Ka < K_3 a \simeq 4.761$ there are again no allowed energy values, i.e. there is an energy gap of width

$$\Delta E_g = \frac{\hbar^2}{2m}\left(K_3^2 - K_2^2\right) \simeq \frac{\hbar^2}{2ma^2}\left(4.761^2 - \pi^2\right)$$

between the lowest energy band and the next energy band. Between $K_3 a \leq Ka \leq K_4 a = 2\pi$ the energy increases from $\hbar^2 K_3^2/2m$ to $\hbar^2 K_4^2/2m$, while $|ka|$ decreases from $|ka| = \pi$ to $ka = 0$. This behavior occurs over and over again, with decreasing energy gaps ΔE_g between adajacent bands. The three lowest energy bands $E_n(k)$ for $u = 5$ are plotted in Figure 10.2.
The energy bands have extrema in the center and at the boundaries of the Brillouin zone,

$$\left.\frac{dE_n(k)}{dk}\right|_{k=0,\pm\pi/a} = \left.\frac{\hbar^2 K_n(k)}{m}\,\frac{dK_n(k)}{dk}\right|_{k=0,\pm\pi/a} = 0.$$

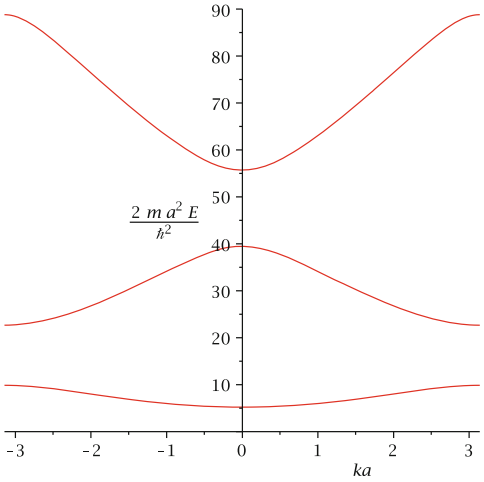


Figure 10.2: The three lowest energy bands $E_0(k)$, $E_1(k)$ and $E_2(k)$ for $u = 5$.

Therefore we can use parabolic approximations

$$E_n(k) \simeq E_n(k_0) \pm \frac{\hbar^2}{2m_n(k_0)}(k - k_0)^2 \tag{10.33}$$

near those extrema, with effective masses

$$\frac{1}{m_n(k_0)} = \pm\frac{1}{\hbar^2}\left.\frac{dE_n(k)}{dk}\right|_{k=k_0} = \pm\frac{K_n(k_0)}{m}\left.\frac{d^2K_n(k)}{dk^2}\right|_{k=k_0}. \tag{10.34}$$

This is denoted as an effective electron mass if the extremum is a minimum, because the required energy to accelerate an electron from the band minimum $\hbar k_0$ to a nearby pseudomomentum $\hbar k$ is $\hbar^2(\Delta k)^2/2m_n(k_0)$. On the other hand, if the extremum is a maximum, the effective mass is denoted as a hole mass, because in that case $\hbar^2(\Delta k)^2/2m_n(k_0)$ is the required energy to move an electron from a nearby point k to k_0 (if that state was vacant), or equivalently move the vacant state (or hole) from k_0 to the nearby point k.
Note that the curvature in the minimum $k_0 = 0$ of the lowest energy band is smaller than in the vacuum, where we would have the parabola $2mEa^2/\hbar^2 = (ka)^2$ in figure 10.2. This means that the effective electron mass in the lowest band satisfies $m_{n=0}(0) > m$. However, band curvature increases for the higher bands, which means small effective masses for higher n.

10.5 kp perturbation theory and effective mass

The combination of the Bloch theorem with second order perturbation theory provides another beautiful introduction to the concept of effective electron or

hole mass in materials. This is a little more technical, but also more general in the sense that it does not rely on a particular potential model.
The starting point for kp perturbation theory is an effective Schrödinger equation for the Bloch factors $u_n(k,x) = \langle x|E_n(k)\rangle$. The identity

$$\mathrm{p}^2|E_n,k\rangle = |k\rangle(\mathrm{p}+\hbar k)^2|E_n(k)\rangle$$

implies the following effective Schrödinger equation for the Bloch factors:

$$\left(\frac{\mathrm{p}^2}{2m}+\frac{\hbar}{m}k\mathrm{p}+V(\mathrm{x})\right)|E_n(k)\rangle = \left(E_n(k)-\frac{\hbar^2k^2}{2m}\right)|E_n(k)\rangle. \tag{10.35}$$

Now suppose that we know the Bloch factors and energy levels at a point k_0 in the Brillouin zone, and we take these solutions of

$$\left(\frac{\mathrm{p}^2}{2m}+\frac{\hbar}{m}k_0\mathrm{p}+V(\mathrm{x})\right)|E_n(k_0)\rangle = \left(E_n(k_0)-\frac{\hbar^2k_0^2}{2m}\right)|E_n(k_0)\rangle \tag{10.36}$$

as 0-th order approximation to the perturbative solution of equation (10.35),

$$\left(\frac{\mathrm{p}^2}{2m}+\frac{\hbar}{m}k_0\mathrm{p}+V(\mathrm{x})+\frac{\hbar}{m}(k-k_0)\mathrm{p}\right)|E_n(k)\rangle = \left(E_n(k)-\frac{\hbar^2k^2}{2m}\right)|E_n(k)\rangle,$$

i.e. the perturbatively sought states and eigenvalues are $|E_n(k)\rangle$ and $E_n(k)-\frac{\hbar^2k^2}{2m}$, and the perturbation operator is $\frac{\hbar}{m}(k-k_0)\mathrm{p}$.
The energy levels in second order perturbation theory are therefore

$$\begin{aligned}E_n(k) = {} & E_n(k_0)+\frac{\hbar^2}{2m}\big(k^2-k_0^2\big)+\frac{\hbar}{m}(k-k_0)\langle E_n(k_0)|\mathrm{p}|E_n(k_0)\rangle \\ & +\frac{\hbar^2}{m^2}(k-k_0)^2\sum_{m\neq n}\frac{|\langle E_m(k_0)|\mathrm{p}|E_n(k_0)\rangle|^2}{E_n(k_0)-E_m(k_0)},\end{aligned}$$

and the effective mass near an extremum k_0 in the n-th band is then in second order perturbation theory

$$\frac{1}{m_n(k_0)} = \frac{1}{\hbar^2}\frac{d^2}{dk^2}E_n(k)\bigg|_{k=k_0} = \frac{1}{m}+\frac{2}{m^2}\sum_{m\neq n}\frac{|\langle E_m(k_0)|\mathrm{p}|E_n(k_0)\rangle|^2}{E_n(k_0)-E_m(k_0)}.$$

If there appear degeneracies between different bands at $k=k_0$, we should split the band indices $n\to i,\alpha$, and we have to apply the result (9.24) to find

$$\begin{aligned}E_{i,\alpha}(k) = {} & E_i(k_0)+\frac{\hbar^2}{2m}\big(k^2-k_0^2\big)+\frac{\hbar}{m}(k-k_0)\langle u_{i,\alpha}(k_0)|\mathrm{p}|u_{i,\alpha}(k_0)\rangle \\ & +\frac{\hbar^2}{m^2}(k-k_0)^2\sum_{j\neq i}\sum_{\beta}\frac{|\langle u_{j,\beta}(k_0)|\mathrm{p}|u_{i,\alpha}(k_0)\rangle|^2}{E_i(k_0)-E_j(k_0)},\end{aligned}$$

$$\frac{1}{m_{i,\alpha}(k_0)} = \frac{1}{\hbar^2}\frac{d^2}{dk^2}E_{i,\alpha}(k)\bigg|_{k=k_0} = \frac{1}{m}+\frac{2}{m^2}\sum_{j\neq i}\sum_{\beta}\frac{|\langle u_{j,\beta}(k_0)|\mathrm{p}|u_{i,\alpha}(k_0)\rangle|^2}{E_i(k_0)-E_j(k_0)}.$$

These results indicate that the effective mass in the lowest energy band is always larger than the free electron mass m, in agreement with our observation from the Kronig-Penney model.

10.6 Problems

10.1 Show that the momentum per lattice site in the Bloch function $\psi_n(k,x)$,

$$\langle p\rangle_{n,k} = \frac{2\pi}{a}\int_{\nu a}^{(\nu+1)a} dx\, \psi_n^+(k,x)\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\psi_n(k,x).$$

is independent of ν and is given in terms of a weighted sum over equivalent sites in the dual lattice,

$$\langle p\rangle_{n,k} = a\sum_\ell \hbar\Big(k+\frac{2\pi}{a}\ell\Big)\left|u_{n,0}\Big(k+\frac{2\pi\ell}{a}\Big)\right|^2.$$

10.2 Show that the Wannier functions $w_{n,\nu}(x) = w_{n,0}(x-\nu a)$ in the lattice and the dual Wannier functions $u_{n,-\ell}(k) = u_{n,0}(k-(2\pi/a)\ell)$ in the dual lattice are related according to

$$w_{n,\nu}(x) = \frac{a}{2\pi}\int_{-\pi/a}^{\pi/a} dk \sum_\ell u_{n,-\ell}(k)\exp\left[\mathrm{i}\Big(k-\frac{2\pi}{a}\ell\Big)(x-\nu a)\right],$$

$$u_{n,-\ell}(k) = \frac{1}{a}\int_0^a dx\sum_\nu w_{n,\nu}(x)\exp\left[-\mathrm{i}\Big(k-\frac{2\pi}{a}\ell\Big)(x-\nu a)\right].$$

Furthermore, show that these relations are equivalent to (10.19).

10.3 Show that we can write the (non-normalized) positive energy Bloch functions for the Kronig-Penney model in Section 10.4 in the form

$$\begin{aligned}\psi_K(k,x) = \langle x|E,k\rangle = \sqrt{\frac{a}{2\pi}}\sum_{q\in\mathbb{Z}}\Theta(x+a-qa)\Theta(qa-x)\exp[\mathrm{i}(q-1)ka]\\ \times\Big(\exp[\mathrm{i}K(x-qa)]-\exp[\mathrm{i}K(x-qa)]\exp[\mathrm{i}(k+K)a]\\ -\exp[-\mathrm{i}K(x-qa)]+\exp[-\mathrm{i}K(x-qa)]\exp[\mathrm{i}(k-K)a]\Big).\end{aligned} \tag{10.37}$$

We use the label $K \equiv K(n,k) = \sqrt{2mE_n(k)}/\hbar$ instead of the energy band index n. The omitted normalization factor N_K is given by

$$\begin{aligned}N_K^{-2} &= 4a[1-\cos(Ka)\cos(ka)] + \frac{4}{K}\sin(Ka)[\cos(ka)-\cos(Ka)]\\ &= 4a\sin(Ka)\left[\sin(Ka)\left(1+\frac{u}{K^2a^2}\right)-\frac{u}{Ka}\cos(Ka)\right].\end{aligned} \tag{10.38}$$

Determine the Bloch factor $u_K(k,x)$ and the dual Wannier states $u_{K,\ell}(k)$ for the Bloch function (10.37).

10.4 Analyze the Bloch functions and Wannier functions for vanishing potential $u = 0$.

Show that the solutions for the energy levels for k in the first Brillouin zone are given by

$$\frac{\sqrt{2mE_n(k)}}{\hbar} \equiv K_n(k) = |k| + \frac{2\pi}{a}n, \quad n = 0, 1, \ldots$$

Using (10.37) with the normalization factor included, construct the Bloch functions $\psi_n(k, x)$ and Bloch factors $u_n(k, x)$ for k in the first Brillouin zone. Show that the Bloch factors in the whole dual lattice are given by

$$u_n(k,x) = \frac{1}{\mathrm{i}\sqrt{a}} \sum_{\ell\in\mathbb{Z}} \left[\Theta\left(k - \frac{2\pi}{a}\ell\right) \Theta\left((2\ell+1)\frac{\pi}{a} - k\right) \exp\left(2\pi\mathrm{i}\frac{n-\ell}{a}x\right) \right.$$
$$\left. + \Theta\left(k - (2\ell-1)\frac{\pi}{a}\right) \Theta\left(\frac{2\pi}{a}\ell - k\right) \exp\left(-2\pi\mathrm{i}\frac{n+\ell}{a}x\right) \right].$$

Show that Wannier functions are given by

$$w_{n,0}(x) = \frac{\sqrt{a}}{\mathrm{i}\pi} \frac{\sin[(2n+1)\pi x/a] - \sin[2n\pi x/a]}{x}.$$

For examples of this, see Figures 10.3 and 10.4.

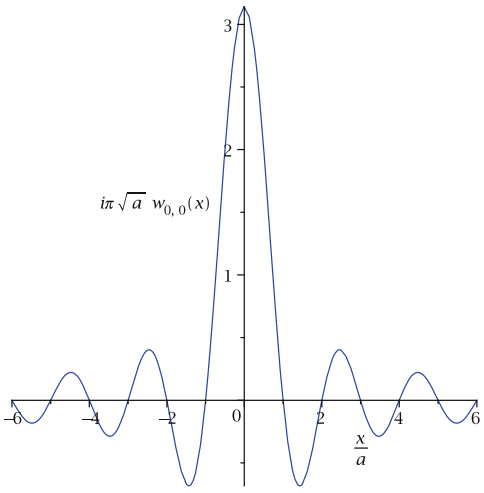


Figure 10.3: The function $w_{0,0}(x)$ for $u = 0$.

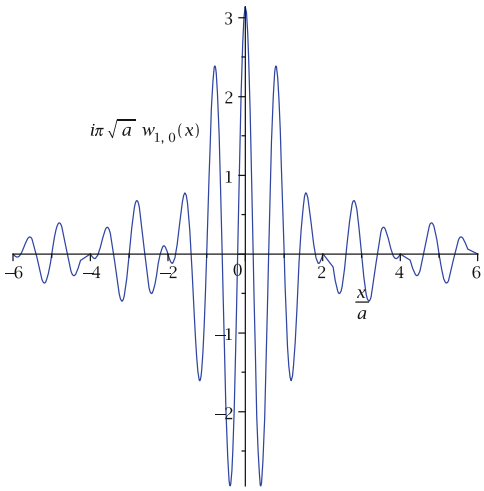


Figure 10.4: The function $w_{1,0}(x)$ for $u = 0$.

10.5 Show that the time-dependent Bloch functions in the whole dual lattice are given for $u = 0$ by

$$\begin{aligned}\psi_n(k,x,t) = \frac{\exp(\mathrm{i}kx)}{\mathrm{i}\sqrt{2\pi}} \sum_{\ell\in\mathbb{Z}} \Bigg[&\Theta\Big(k - \frac{2\pi}{a}\ell\Big)\,\Theta\Big((2\ell+1)\frac{\pi}{a} - k\Big) \\ &\times \exp\Big(2\pi\mathrm{i}\frac{n-\ell}{a}x\Big) \exp\Bigg[-\frac{\mathrm{i}\hbar t}{2m}\Big(k + 2\pi\frac{n-\ell}{a}\Big)^2\Bigg] \\ &+ \Theta\Big(k - (2\ell-1)\frac{\pi}{a}\Big)\,\Theta\Big(\frac{2\pi}{a}\ell - k\Big) \exp\Big(-2\pi\mathrm{i}\frac{n+\ell}{a}x\Big) \\ &\times \exp\Bigg[-\frac{\mathrm{i}\hbar t}{2m}\Big(k - 2\pi\frac{n+\ell}{a}\Big)^2\Bigg]\Bigg].\end{aligned}$$

Show that the time-dependent Wannier functions (10.23) are given by

$$\begin{aligned}w_{n,0}(x,t) = -\sqrt{\frac{\mathrm{i}ma}{8\pi\hbar t}} \exp\Big(\mathrm{i}\frac{mx^2}{2\hbar t}\Big) \Bigg[&\mathrm{erf}\Bigg(-\sqrt{\mathrm{i}\frac{mx^2}{2\hbar t}} - 2n\pi\sqrt{\frac{\mathrm{i}\hbar t}{2ma^2}}\Bigg) \\ &-\mathrm{erf}\Bigg(-\sqrt{\mathrm{i}\frac{mx^2}{2\hbar t}} - (2n+1)\pi\sqrt{\mathrm{i}\frac{\hbar t}{2ma^2}}\Bigg) \\ &+\mathrm{erf}\Bigg(-\sqrt{\mathrm{i}\frac{mx^2}{2\hbar t}} + (2n+1)\pi\sqrt{\frac{\mathrm{i}\hbar t}{2ma^2}}\Bigg) \\ &-\mathrm{erf}\Bigg(-\sqrt{\mathrm{i}\frac{mx^2}{2\hbar t}} + 2n\pi\sqrt{\frac{\mathrm{i}\hbar t}{2ma^2}}\Bigg)\Bigg],\end{aligned}$$

where $\sqrt{\mathrm{i}} = (1+\mathrm{i})/\sqrt{2}$.

10.6 Figures 10.5 and 10.6 illustrate the conditions (10.32) and (10.30) for existence of negative or positive energies for $u = -3$.

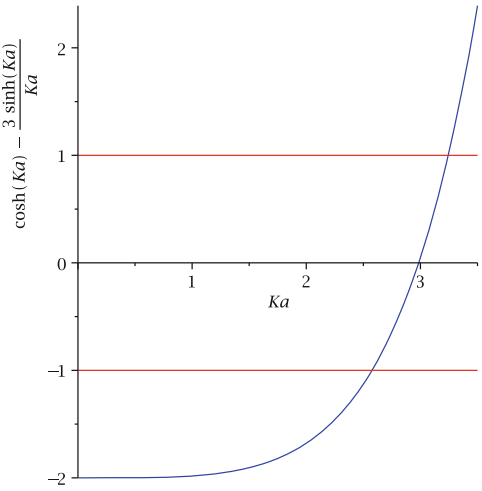


Figure 10.5: The function $g(Ka) = \cosh(Ka) - (3/Ka)\sinh(Ka)$. Only values of Ka with $|g(Ka)| \leq 1$ correspond to allowed energy values $E = -\hbar^2 K^2/2m$ in the Kronig-Penney model with $u = -3$.

Note that for the negative energies increasing K corresponds to decreasing E. Therefore the energy minimum in the negative energy band arises from $g(Ka) = 1$, $ka = 0$, and the maximum in the negative energy band arises from $g(Ka) = -1$, $ka = \pm\pi$ in Figure 10.5. Analyze the band structure in this model similar to the analysis of Figure 10.1. Contrary to the case of positive u, there are also negative energy values possible for $u = -3$. How many negative energy bands are there for $u = -3$?

10.7 Figures 10.7 and 10.8 illustrate the conditions (10.32) and (10.30) for existence of negative or positive energies for $u = -1.5$.
Analyze the band structure in this model similar to the analysis of Problem 10.6. Contrary to the case $u < -2$, we reach the value $E = 0$ for $Ka = 0$ in figure 10.7 for $0 < |ka| < \pi$. At this point we go into the positive energies corresponding to the values $0 \leq Ka \lesssim 1.689$ in figure 10.8, i.e. the lowest energy band contains both negative and positive energies in this case. For which value of ka is $E = 0$?

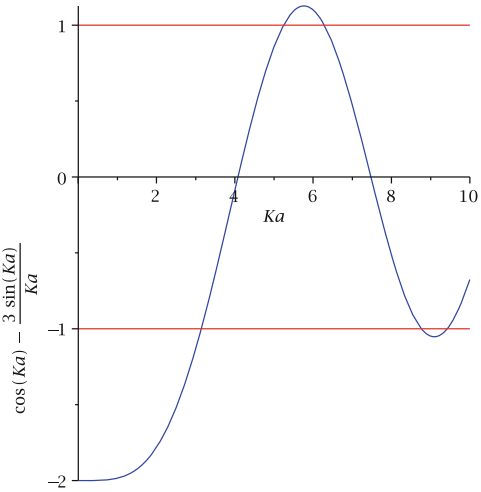


Figure 10.6: The function $f(Ka) = \cos(Ka) - (3/Ka)\sin(Ka)$. Only values of Ka with $|f(Ka)| \leq 1$ correspond to allowed energy values $E = \hbar^2 K^2/2m$ in the Kronig-Penney model with $u = -3$.

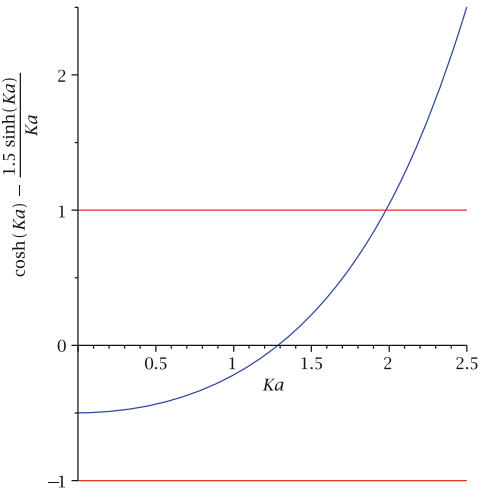


Figure 10.7: The function $g(Ka) = \cosh(Ka) - (1.5/Ka)\sinh(Ka)$. Only values of Ka with $|g(Ka)| \leq 1$ correspond to allowed energy values $E = -\hbar^2 K^2/2m$ in the Kronig-Penney model with $u = -1.5$

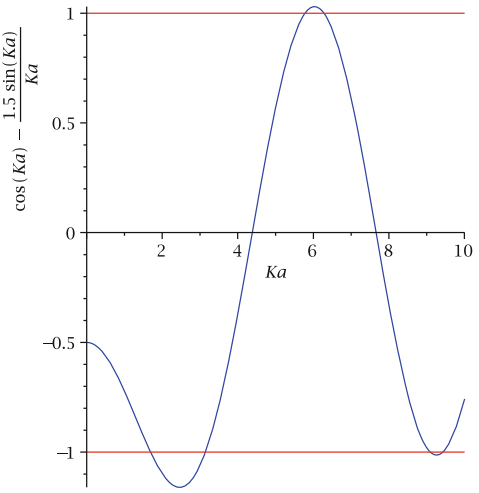


Figure 10.8: The function $f(Ka) = \cos(Ka) - (1.5/Ka)\sin(Ka)$. Only values of Ka with $|f(Ka)| \leq 1$ correspond to allowed energy values $E = \hbar^2 K^2/2m$ in the Kronig-Penney model with $u = -1.5$.

Chapter 11

Scattering Off Potentials

Most two-particle interaction potentials $V(\boldsymbol{x}_1 - \boldsymbol{x}_2)$ assume a finite value V_∞ if $|\boldsymbol{x}_1 - \boldsymbol{x}_2| \to \infty$. If the relative motion of the two-particle system has an energy $E > V_\infty$ the particles can have arbitrary large distance. In particular, we can imagine a situation where the two particles approach each other from an initially large separation and after reaching some minimal distance move away from each other. The force between the two particles will influence the trajectories of the two particles, and this influence will be strongest when the particles are close together. The deflection of particle trajectories due to interaction forces is denoted as scattering. This is denoted as potential scattering if the interaction forces between the particles can be expressed through a potential. We have seen in Section 7.1 that the motion of two particles with an interaction potential of the form $V(\boldsymbol{r}) = V(\boldsymbol{x}_1 - \boldsymbol{x}_2)$ can be separated into center of mass motion and relative motion

$$E\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{r}) + V(\boldsymbol{r})\psi(\boldsymbol{r}). \tag{11.1}$$

Here I wrote m for the reduced mass of the two-particle system.

Equation (11.1) with $E > V_\infty$ does not only describe two-particle scattering, but also scattering of a particle of mass m off a potential with fixed center $r = 0$, e.g. because the source of the potential is fixed by forces which do not affect the scattered particle.

Scattering is an important technique for the determination of physical properties. Within the framework of potential scattering, observations of deflections of particle trajectories in a potential can be used to determine the strength and functional dependence $V(\boldsymbol{r})$ of a scattering potential.

Suppose that we wish to determine a scattering potential $V(\boldsymbol{r})$ through scattering of non-relativistic particles of momentum $\hbar\boldsymbol{k}$ off the potential. The deflected particles will have momenta $\boldsymbol{k}' \neq \boldsymbol{k}$, and one observable that we should certainly be able to measure is the number $dn(\Omega)/dt$ of particles per time which are deflected into a small solid angle $d\Omega = d\vartheta d\varphi \sin\vartheta$ in the direction $\hat{\boldsymbol{x}} = (\sin\vartheta\,\cos\varphi, \sin\vartheta\,\sin\varphi, \cos\vartheta)$. According to the definition of particle

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current densities j, this number will be given by

$$\frac{dn(\Omega)}{dt} = \lim_{r\to\infty} j_{out}(\hat{\boldsymbol{k}}')r^2 d\Omega,$$

where $j_{out}(\hat{\boldsymbol{k}}')$ is the number of deflected particles per area and per time which are moving in the direction $\hat{\boldsymbol{k}}' = \hat{\boldsymbol{x}}$. We are taking the limit $r \to \infty$ because we are interested in measuring $dn(\Omega)/dt$ far from the scattering center (or for large separation of particles in particle-particle scattering), to make sure that the scattering potential does not deflect the scattered particles any further.
The number of particles $dn(\Omega)/dt$ which are scattered into the direction $\hat{\boldsymbol{k}}' = \hat{\boldsymbol{x}}$ is of course proportional to the number $j_{in}(\hat{\boldsymbol{k}})$ of particles per area and per time which are incident on the scattering center, and it is also proportional to the width $d\Omega$ of the solid angle over which we sum the scattered particles. Therefore we expect that the observable which may really tell us something about the scattering potential is gotten by dividing out the trivial dependence on j_{in} and $d\Omega$, i.e. we define

$$\frac{d\sigma}{d\Omega} = \frac{1}{j_{in}(\hat{\boldsymbol{k}})}\frac{dn(\Omega)}{d\Omega dt} = \lim_{r\to\infty} r^2 \frac{j_{out}(\hat{\boldsymbol{k}}')}{j_{in}(\hat{\boldsymbol{k}})}. \tag{11.2}$$

The quantity $d\sigma(\Omega) = (dn(\Omega)/dt)/j_{in}$ has the dimension of an area and is therefore known as a *differential scattering cross section*. Differential scattering cross sections are the primary observables in potential scattering.
If we integrate over all possible scattering directions, we get the *scattering cross section*

$$\sigma = \int d\sigma = \frac{1}{j_{in}(\hat{\boldsymbol{k}})}\int d\Omega \frac{dn(\Omega)}{dt} = \frac{1}{j_{in}(\hat{\boldsymbol{k}})}\frac{dn}{dt},$$

i.e. the scattering cross section is the total number of scattered particles per time, dn/dt, divided by the current density of incident particles.
For an explanation of the name *cross section* we also remark that the calculation of scattering of particles off a hard sphere of radius R in *classical mechanics* yields a scattering cross section $\sigma = \pi R^2$ which equals the cross section of the sphere. We will see below in Section 11.3 that quantum mechanics actually yields a larger scattering cross section of a sphere, e.g. $\sigma = 4\pi R^2$ for scattering of very low energetic particles. Scattering of low energy particles off a sphere could be considered as a most basic illustration of measuring properties of a scattering center. Measuring the number dn/dt of particles per time which are scattered by the sphere and dividing by the incident particle current density provides a measurement of the radius $R = \sqrt{\sigma/4\pi} = \sqrt{(dn/dt)/4\pi j_{in}}$ of the scattering center.
The particle current density of particles described by a wave function $\psi(\boldsymbol{x}, t)$ will be proportional to the corresponding probability current density

$$\boldsymbol{j} = \frac{\hbar}{2im}\left(\psi^+ \cdot \boldsymbol{\nabla}\psi - \boldsymbol{\nabla}\psi^+ \cdot \psi\right),$$

and therefore we can use probability current densities in the calculation of the ratio in (11.2).

11.1 The free energy dependent Green's function

Many applications of quantum mechanics require the calculation of the inverse (or resolvent) $\mathcal{G}(E)$ of the operator $E - H_0 = E - (\mathbf{p}^2/2m)$,

$$(E - H_0)\mathcal{G}(E) = 1.$$

E.g. if we consider a time-independent potential V, the time-independent Schrödinger equation

$$(E - H_0)|\psi(E)\rangle = V|\psi(E)\rangle \tag{11.3}$$

is equivalent to

$$|\psi(E)\rangle = |\psi_0(E)\rangle + \mathcal{G}(E)V|\psi(E)\rangle, \tag{11.4}$$

where $|\psi_0(E)\rangle$ is a solution of $(E - H_0)|\psi_0(E)\rangle = 0$. Iteration of (11.4) then yields the perturbation series

$$|\psi(E)\rangle = \sum_{n=0}^{\infty} [\mathcal{G}(E)V]^n \, |\psi_0(E)\rangle. \tag{11.5}$$

For potential scattering theory it is customary to rescale $\mathcal{G}(E)$ by a factor $-\hbar^2/2m$, such that the zero energy Green's function $G(0)$ is the inverse of the negative Laplace operator. The equation

$$\mathcal{G}(E) = -\frac{2m}{\hbar^2}G(E) = \frac{1}{E - H_0 + \mathrm{i}\epsilon}, \quad \epsilon \to +0, \tag{11.6}$$

is then in $\boldsymbol{x}$-representation

$$\Delta G(\boldsymbol{x} - \boldsymbol{x}', E) + \frac{2m}{\hbar^2}EG(\boldsymbol{x} - \boldsymbol{x}', E) = -\delta(\boldsymbol{x} - \boldsymbol{x}'). \tag{11.7}$$

Here we defined the $\boldsymbol{x}$-representation $G(\boldsymbol{x}, \boldsymbol{x}'; E) \equiv \langle \boldsymbol{x}|G(E)|\boldsymbol{x}'\rangle$ of the energy-dependent Green's function and used the fact that the differential equation for $G(\boldsymbol{x}, \boldsymbol{x}'; E)$ is translation invariant. The shift $\mathrm{i}\epsilon \to +\mathrm{i}0$ in equation (11.7) defines the *retarded Green's function* for the Schrödinger equation. The reason for this terminology is that the corresponding Green's function in the time domain

$$\mathcal{G}(t) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dE\, \mathcal{G}(E) \exp\left(-\frac{\mathrm{i}}{\hbar}Et\right) = \frac{\Theta(t)}{\mathrm{i}\hbar}\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t\right) \tag{11.8}$$

satisfies the conditions

$$\mathrm{i}\hbar\frac{\partial\mathcal{G}(t)}{\partial t} - H_0\mathcal{G}(t) = \delta(t), \quad \mathcal{G}(t)\Big|_{t<0} = 0.$$

This implies that $\mathcal{G}$ propagates time-dependent perturbations

$$\mathrm{i}\hbar\frac{\partial}{\partial t}|\psi(t)\rangle - H_0|\psi(t)\rangle = V(t)|\psi(t)\rangle$$

forward in time,

$$\begin{aligned}|\psi(t)\rangle &= |\psi_0(t)\rangle + \int_{-\infty}^{\infty} dt'\, \mathcal{G}(t-t')V(t')|\psi(t')\rangle \\ &= |\psi_0(t)\rangle - \frac{\mathrm{i}}{\hbar}\int_{-\infty}^{t} dt'\, \exp\left(-\frac{\mathrm{i}}{\hbar}H_0(t-t')\right)V(t')|\psi(t')\rangle. \end{aligned} \tag{11.9}$$

We will revisit time-dependent perturbations in Chapter 13, and focus on scattering due to time-independent perturbations (11.3-11.5) for now.
We first calculate the Green's function $G(\boldsymbol{x}, E)$ for $E = \hbar^2k^2/2m > 0$, and we suppress the fixed variable E in the notation. We can convert the condition

$$(\Delta + k^2)G(\boldsymbol{x}) = -\delta(\boldsymbol{x})$$

into an algebraic condition through substitution of the Fourier transforms

$$G(\boldsymbol{x}) = \frac{1}{(2\pi)^{3/2}}\int d^3\boldsymbol{\kappa}\, G(\boldsymbol{\kappa})\exp(\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{x}), \quad \delta(\boldsymbol{x}) = \frac{1}{(2\pi)^3}\int d^3\boldsymbol{\kappa}\, \exp(\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{x}).$$

This yields with the retardation prescription from (11.6)

$$G(\boldsymbol{\kappa}) = \frac{1}{(2\pi)^{3/2}}\frac{1}{\kappa^2 - k^2 - \mathrm{i}\epsilon}$$

and

$$\begin{aligned} G(\boldsymbol{x}) &= \frac{1}{(2\pi)^3}\int d^3\boldsymbol{\kappa}\, \frac{\exp(\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{x})}{\kappa^2 - k^2 - \mathrm{i}\epsilon} = \frac{1}{(2\pi)^2}\int_{-1}^{1} d\xi \int_0^{\infty} d\kappa\, \kappa^2 \frac{\exp(\mathrm{i}\kappa r\xi)}{\kappa^2 - k^2 - \mathrm{i}\epsilon} \\ &= \frac{1}{(2\pi)^2 \mathrm{i}r}\int_0^{\infty} d\kappa\, \kappa \frac{\exp(\mathrm{i}\kappa r) - \exp(-\mathrm{i}\kappa r)}{\kappa^2 - k^2 - \mathrm{i}\epsilon} \\ &= \frac{1}{(2\pi)^2 \mathrm{i}r}\int_{-\infty}^{\infty} d\kappa\, \kappa \frac{\exp(\mathrm{i}\kappa r)}{\kappa^2 - k^2 - \mathrm{i}\epsilon}. \end{aligned}$$

Due to $r > 0$, we have to close the integration path in the upper complex κ plane if we want to use the residue theorem see Figure 11.1. Decomposing the denominator into its simple poles

$$\frac{1}{\kappa^2 - k^2 - \mathrm{i}\epsilon} = \frac{1}{(\kappa - k - \mathrm{i}\epsilon)(\kappa + k + \mathrm{i}\epsilon)}$$

then yields

$$G(\boldsymbol{x}) = \frac{1}{2\pi r}\frac{\kappa\exp(\mathrm{i}\kappa r)}{\kappa + k}\bigg|_{\kappa=k} = \frac{1}{4\pi r}\exp(\mathrm{i}kr), \tag{11.10}$$

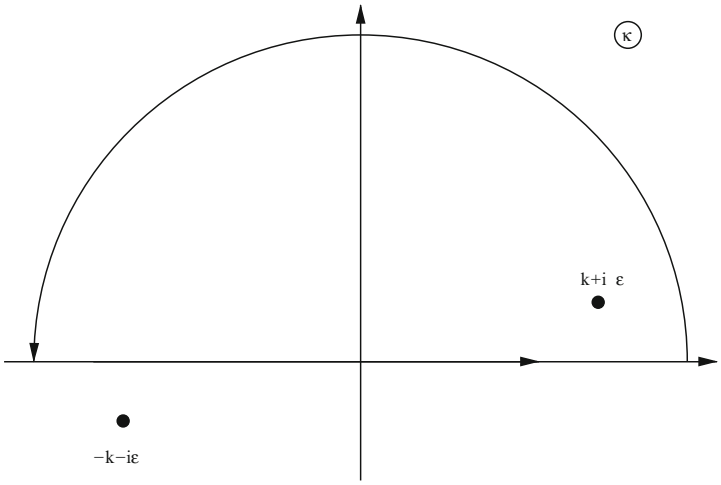


Figure 11.1: Location of the poles and integration contour in the complex κ plane

i.e. the retardation requirement $\mathcal{G}(t) \propto \Theta(t)$ yields only outgoing spherical waves for positive energy.
If we perform the same calculation for $E = -\hbar^2 k^2/2m < 0$, $k > 0$, we find a denominator

$$\frac{1}{\kappa^2 + k^2} = \frac{1}{(\kappa - \mathrm{i}k)(\kappa + \mathrm{i}k)}$$

and integration yields

$$G(\boldsymbol{x}) = \frac{1}{4\pi r} \exp(-kr). \tag{11.11}$$

We can combine the results for positive and negative energy into

$$G(\boldsymbol{x}, E) = \frac{\Theta(E)}{4\pi r} \exp\Big(\mathrm{i}\sqrt{2mE}\frac{r}{\hbar}\Big) + \frac{\Theta(-E)}{4\pi r} \exp\Big(-\sqrt{-2mE}\frac{r}{\hbar}\Big). \tag{11.12}$$

11.2 Potential scattering in the Born approximation

We consider a particle of energy $E = \hbar^2 k^2/2m$ in a static potential $V(\boldsymbol{x})$ of finite range. The time-independent Schrödinger equation

$$(\Delta + k^2)\psi(\boldsymbol{x}) = \frac{2m}{\hbar^2} V(\boldsymbol{x})\psi(\boldsymbol{x}) \tag{11.13}$$

can be converted into an integral equation using the Green's function (11.10),

$$\begin{aligned}\psi(\boldsymbol{x}) &= \frac{\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})}{(2\pi)^{3/2}} - \frac{m}{2\pi\hbar^2}\int d^3\boldsymbol{x}'\,\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\exp(\mathrm{i}k|\boldsymbol{x}-\boldsymbol{x}'|)V(\boldsymbol{x}')\psi(\boldsymbol{x}') \\ &\approx \frac{\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})}{(2\pi)^{3/2}} - \frac{m}{(2\pi)^{5/2}\hbar^2}\int d^3\boldsymbol{x}'\,\frac{V(\boldsymbol{x}')}{|\boldsymbol{x}-\boldsymbol{x}'|}\exp(\mathrm{i}k|\boldsymbol{x}-\boldsymbol{x}'| + \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}'),\end{aligned} \tag{11.14}$$

where we simply reinserted the leading plane wave term for $\psi(\boldsymbol{x}')$ in the integrand. We will neglect an irrelevant normalization factor $(2\pi)^{-3/2}$ in the following, because finally we are only interested in the ratio of the different parts of the wave function.
For $r \gg r'$ we have

$$|\boldsymbol{x}-\boldsymbol{x}'| \approx \sqrt{r^2 - 2rr'\cos\theta} \approx r - r'\cos\theta = r - \frac{1}{r}\boldsymbol{x}\cdot\boldsymbol{x}' = r - \hat{\boldsymbol{x}}\cdot\boldsymbol{x}'.$$

We need the expansion to this order in the exponent of the Green's function in equation (11.14). However, for the denominator the expansion

$$\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|} \approx \frac{1}{r}$$

will suffice, because the subleading term $(r'/r^2)\cos\theta$ will not contribute to the differential scattering cross section (11.2) due to the limit $\lim_{r\to\infty} r^2 j_{out}$.
Substitution of the approximations yields the *Born approximation*

$$\begin{aligned}\psi(\boldsymbol{x}) &= \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) - \frac{m}{2\pi\hbar^2}\frac{1}{r}\exp(\mathrm{i}kr)\int d^3\boldsymbol{x}'\,\exp[\mathrm{i}(\boldsymbol{k}-k\hat{\boldsymbol{x}})\cdot\boldsymbol{x}']V(\boldsymbol{x}') \\ &= \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) + f(k\hat{\boldsymbol{x}}-\boldsymbol{k})\frac{1}{r}\exp(\mathrm{i}kr) = \psi^{(\mathrm{in})}(\boldsymbol{x}) + \psi^{(\mathrm{out})}(\boldsymbol{x}),\end{aligned} \tag{11.15}$$

with the scattering amplitude

$$f(\Delta\boldsymbol{k}) = -\frac{m}{2\pi\hbar^2}\int d^3\boldsymbol{x}\,\exp(-\mathrm{i}\Delta\boldsymbol{k}\cdot\boldsymbol{x})V(\boldsymbol{x}) = -\sqrt{2\pi}\frac{m}{\hbar^2}V(\Delta\boldsymbol{k}). \tag{11.16}$$

For later reference, we notice that this can also be written as a transition matrix element of the operator $V(\mathbf{x})$,

$$f(\Delta\boldsymbol{k}) = -(2\pi)^2\frac{m}{\hbar^2}\langle\boldsymbol{k}'|V|\boldsymbol{k}\rangle. \tag{11.17}$$

Like in the prototype one-dimensional scattering event described in Section 3.1, the monochromatic asymptotic wave function (11.15) describes both the incident and the scattered particles simultaneously, for the same reasons as in Section 3.1. The current density j_{out} of scattered particles is therefore calculated from the outgoing spherical wave component $\psi^{(\mathrm{out})}(\boldsymbol{x})$ in the wave function (11.15), and we only need the leading term for $r \to \infty$,

$$\begin{aligned}\boldsymbol{j}_{out} &= \frac{\hbar}{2\mathrm{i}m}\left(\psi^{(\mathrm{out})+}\boldsymbol{\nabla}\psi^{(\mathrm{out})} - \boldsymbol{\nabla}\psi^{(\mathrm{out})+}\cdot\psi^{(\mathrm{out})}\right)\Big|_{\text{leading term for } r\to\infty} \\ &= \frac{\hbar k}{m}\frac{\hat{\boldsymbol{x}}}{r^2}|f(k\hat{\boldsymbol{x}}-\boldsymbol{k})|^2.\end{aligned} \tag{11.18}$$

The incoming current density j_{in} is calculated from the incoming plane wave component $\psi^{(\mathrm{in})}(\boldsymbol{x})$,

$$\boldsymbol{j}_{in} = \frac{\hbar \boldsymbol{k}}{m}. \tag{11.19}$$

Both j_{in} and j_{out} come in units of cm/s instead of the expected $\mathrm{cm}^{-2}/\mathrm{s}$ for particle or probability current densities. The reason for this is the use of plane or spherical wave states in $\boldsymbol{k}$ space which are dimensionless in $\boldsymbol{x}$ representation, see Section 5.3. Therefore the current densities (11.18) and (11.19) are current densities per unit of volume in $\boldsymbol{k}$ space. The normalization to $\boldsymbol{k}$ space volume cancels in the ratio j_{out}/j_{in}, and substitution of equations (11.18,11.19) into (11.2) yields

$$\frac{d\sigma_k}{d\Omega} = |f(k\hat{\boldsymbol{x}} - \boldsymbol{k})|^2. \tag{11.20}$$

The scattering amplitude (11.16) for a spherically symmetric potential is

$$\begin{aligned} f_k(\theta) \equiv f(\Delta\boldsymbol{k}) = f(\Delta k) = f[2k\sin(\theta/2)] &= -\frac{2m}{\hbar^2 \Delta k}\int_0^\infty dr\, r \sin(\Delta k r) V(r) \\ &= -\frac{m}{\hbar^2 k \sin(\theta/2)}\int_0^\infty dr\, r \sin[2kr\sin(\theta/2)] V(r), \end{aligned} \tag{11.21}$$

where θ is the scattering angle.

In agreement with the observation that the energy-dependent wave function describes both the incoming and the scattered particles, we have split the wave function $\psi(\boldsymbol{r})$ into the components $\psi^{(\mathrm{in})}(\boldsymbol{r})$ and $\psi^{(\mathrm{out})}(\boldsymbol{r})$, and then calculated separate current densities $\boldsymbol{j}_{in}$ and $\boldsymbol{j}_{out}$ from both contributions rather than calculate a total current density $\boldsymbol{j}$ for $\psi(\boldsymbol{r})$. On the other hand, probability conservation implies for stationary states $\boldsymbol{\nabla}\cdot\boldsymbol{j} = 0$, but only for the full current density including the interference terms $\boldsymbol{j} - \boldsymbol{j}_{in} - \boldsymbol{j}_{out}$ between the incoming and scattered parts of the wave function. Therefore the interference terms will describe reduction of the current of incoming particles due to scattering.

When we discuss this effect on the basis of the wave function (11.15), we have to keep in mind that this is only a large distance approximation which was justified by the observation that we are interested in the large distance limit of $r^2 j_{out}$. Furthermore, the wave function (11.15) will only yield components j_r and j_θ in spherical coordinates, and only j_r will be relevant for the detailed balance between incoming and scattered particles. The radial current density from (11.15) for $kr \gg 1$ and neglecting terms which drop off faster than r^{-2} is

$$\begin{aligned} \frac{m}{\hbar} j_r &= \Im\left(\psi^+ \frac{\partial}{\partial r}\psi\right) \simeq k\cos\theta + k\frac{|f_k(\theta)|^2}{r^2} \\ &\quad + \frac{k}{r}\Re\big(f_k(\theta)\exp[\mathrm{i}kr(1-\cos\theta)] + f_k^+(\theta)\cos\theta\exp[-\mathrm{i}kr(1-\cos\theta)]\big)\,. \end{aligned}$$

Conservation of particles requires $\int d\Omega\, r^2 j_r = 0$. The first term cancels in the integration over the sphere at radius r with $r^2 \sin\theta\, d\theta\, d\varphi$, and the remaining terms yield with $u = 1 - \cos\theta$, $F_k(u) = f_k(\theta)$,

$$k\sigma_k + 2\pi kr \int_0^2 du\, \Re\big[F_k(u)\exp(\mathrm{i}kru) + F_k^+(u)(1-u)\exp(-\mathrm{i}kru)\big] = 0. \tag{11.22}$$

Here $\sigma_k \equiv \int d\Omega\, d\sigma_k/d\Omega$ is the total scattering cross section.
Two-fold partial integration yields

$$\begin{aligned} kr\int_0^2 du\, F_k(u)\exp(\mathrm{i}kru) = {} & \mathrm{i}F_k(0) - \mathrm{i}F_k(2)\exp(2\mathrm{i}kr) - \frac{1}{kr}F_k'(0) \\ & + \frac{1}{kr}F_k'(2)\exp(2\mathrm{i}kr) \\ & - \frac{1}{kr}\int_0^2 du\, F_k''(u)\exp(\mathrm{i}kru). \end{aligned}$$

The last three terms vanish for $kr \to \infty$. For the term $F_k(2)\exp(2\mathrm{i}kr)$ we observe that averaging over a very small momentum uncertainty $\Delta k/k = \pi/kr \ll 1$ also yields a null result, because it corresponds to an integration in k space over a range $-\pi/r \le k \le \pi/r$. This can be understood physically as destructive interference between states with a minute variation in momentum. Therefore we find for $kr \to \infty$

$$kr\int_0^2 du\, F_k(u)\exp(\mathrm{i}kru) \to \mathrm{i}f_k(0).$$

In the same way one finds

$$kr\int_0^2 du\, F_k^+(u)(1-u)\exp(-\mathrm{i}kru) \to -\mathrm{i}f_k^+(0),$$

and equation (11.22) yields in the large kr limit the *optical theorem*

$$\sigma_k = \frac{4\pi}{k}\Im f_k(0) \tag{11.23}$$

between the total scattering cross section and the imaginary part of the scattering amplitude in forward direction.

11.3 Scattering off a hard sphere

The hard sphere of radius R corresponds to the $V_0 \to \infty$ limit of a potential $V(r) = V_0\Theta(R-r)$. This reduces to the solution of the free Schrödinger equation for $r > R$ and a boundary condition on the surface of the sphere,

$$\psi(\boldsymbol{r})\Big|_{r=R} = 0. \tag{11.24}$$

We recall that the radial Schrödinger equation for a free particle with fixed angular momentum M_z, $\boldsymbol{M}^2$ and energy $E = \hbar^2 k^2/2m$ yields the radial equation (7.40),

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2\right) r\psi(r) = 0. \tag{11.25}$$

We have seen in Section 7.8 that the regular solutions for arbitrary ℓ can be gotten through repeated application of $r^{-1}d/dr$ on the regular solution for $\ell = 0$,

$$\psi^{(\mathrm{in})}_{\ell,k}(r) \propto j_\ell(kr), \quad j_\ell(x) = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell j_0(x), \quad j_0(x) = \frac{\sin x}{x}.$$

We denote the regular solutions $j_\ell(kr)$ as $\psi^{(\mathrm{in})}_{\ell,k}(r)$, because we can superimpose those functions according to equation (7.46) to form an incoming plane wave. However, equation (11.25) also has an outgoing radial wave as a solution for $\ell = 0$,

$$\psi^{(\mathrm{out})}_{0,k}(r) \propto \frac{\exp(\mathrm{i}kr)}{kr} = -\mathrm{i}h^{(1)}_0(kr).$$

The reasoning leading to equations (7.41, 7.42) also implies that repeated application of $r^{-1}d/dr$ on the outgoing radial wave solution leads to solutions for higher ℓ,

$$\psi^{(\mathrm{out})}_{\ell,k}(r) \propto -\mathrm{i}h^{(1)}_\ell(kr), \quad h^{(1)}_\ell(x) = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell h^{(1)}_0(x).$$

In leading order in $1/r$, these are again outgoing radial waves,

$$h^{(1)}_\ell(kr) \simeq (-)^\ell \frac{\exp(\mathrm{i}kr)}{\mathrm{i}kr}. \tag{11.26}$$

The functions $h^{(1)}_\ell(x)$ are known as spherical Hankel functions of the first kind. We can use the spherical Bessel and Hankel functions to form solutions of equation (11.25) which satisfy the condition (11.24) and contain an outgoing spherical wave in the asymptotic limit,

$$\psi_{\ell,k}(r) = \psi^{(\mathrm{in})}_{\ell,k}(r) + \psi^{(\mathrm{out})}_{\ell,k}(r) \propto j_\ell(kr) - h^{(1)}_\ell(kr)\frac{j_\ell(kR)}{h^{(1)}_\ell(kR)}.$$

However, equation (7.46) then tells us how to write down a solution to the free Schrödinger equation for energy $E = \hbar^2 k^2/2m$ outside of the hard sphere, which satisfies the boundary condition (11.24) and contains both a plane wave and an outgoing spherical wave,

$$\begin{aligned}
\psi_k(\boldsymbol{r}) &= \sum_{\ell=0}^{\infty} (2\ell+1)\mathrm{i}^\ell \left(j_\ell(kr) - h^{(1)}_\ell(kr)\frac{j_\ell(kR)}{h^{(1)}_\ell(kR)}\right) P_\ell(\cos\theta) \\
&= \exp(\mathrm{i}kz) - \sum_{\ell=0}^{\infty} (2\ell+1)\mathrm{i}^\ell h^{(1)}_\ell(kr)\frac{j_\ell(kR)}{h^{(1)}_\ell(kR)} P_\ell(\cos\theta) \\
&= \psi^{(\mathrm{in})}(\boldsymbol{r}) + \psi^{(\mathrm{out})}(\boldsymbol{r}).
\end{aligned} \tag{11.27}$$

From our previous experience in Sections 3.1 and 11.2 we already anticipated that the monochromatic wave function will describe both incoming and scattered particles. According to equation (11.26), the asymptotic expansion of the wave function for large r is

$$\psi_k(\boldsymbol{r}) \simeq \exp(\mathrm{i}kz) + f_k(\theta)\frac{\exp(\mathrm{i}kr)}{r},$$

$$f_k(\theta) = -\frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)(-\mathrm{i})^{\ell+1}P_\ell(\cos\theta)\frac{j_\ell(kR)}{h_\ell^{(1)}(kR)}.$$

The resulting expression for the differential scattering cross section of the hard sphere is a little unwieldy,

$$\frac{d\sigma_k}{d\Omega} = |f_k(\theta)|^2 = \frac{1}{k^2}\sum_{\ell,\ell'=0}^{\infty}(2\ell+1)(2\ell'+1)\mathrm{i}^{\ell-\ell'}P_\ell(\cos\theta)P_{\ell'}(\cos\theta) \times\frac{j_\ell^+(kR)j_{\ell'}(kR)}{h_\ell^{(1)+}(kR)h_{\ell'}^{(1)}(kR)}. \tag{11.28}$$

However, for the scattering cross section the orthogonality property of Legendre polynomials

$$\int_0^\pi d\theta\,\sin\theta\,P_\ell(\cos\theta)P_{\ell'}(\cos\theta) = \frac{2}{2\ell+1}\delta_{\ell,\ell'}$$

yields a much simpler result,

$$\sigma_k = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\left|\frac{j_\ell(kR)}{h_\ell^{(1)}(kR)}\right|^2. \tag{11.29}$$

This is shown in Figure 11.2.
The asymptotic behavior for small arguments kR, $j_\ell(kR) \simeq (kR)^\ell/(2\ell+1)!!$ and $h_\ell^{(1)}(kR) \simeq -\mathrm{i}(2\ell-1)!!(kR)^{-\ell-1}$, imply for the low energy or long wavelength limit $\lambda \gg R$ that only the $\ell = 0$ contribution survives with

$$\lim_{kR\to 0}\sigma_k = 4\pi R^2.$$

The quantum mechanical scattering cross section drops continuously from $\lim_{kR\to 0}\sigma_k = 4\pi R^2$ to $\lim_{kR\to\infty}\sigma_k = 2\pi R^2$, i.e. it always excedes the classical value $\sigma_{cl} = \pi R^2$ by more than a factor of 2. In terms of the variables k and R, σ_k seems to be independent of $\hbar$ and one might naively expect that this is the reason for absence of a classical limit for scattering off a hard sphere, but this is wrong for two reasons. If one compares with classical results one should use the same variables as in classical mechanics, and if in terms of the classical variables the quantum mechanical result is independent of $\hbar$, we rather expect to find the same result as in classical mechanics. Furthermore, when one calculates classical scattering cross sections, one uses the momentum $p = \hbar k$ for the

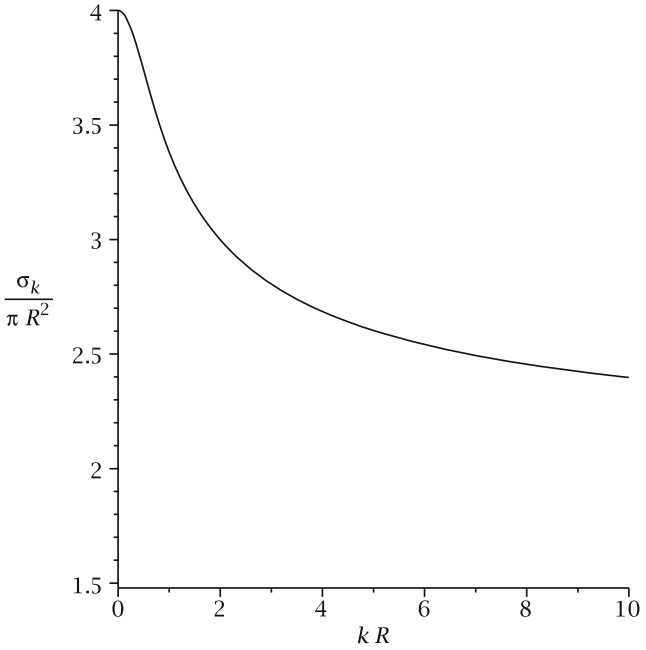


Figure 11.2: The scattering cross section of a hard sphere normalized to the classical scattering cross section $\sigma_{classical} = \pi R^2$.

incident particles as a variable besides the radius R of the sphere, i.e. in terms of classical variables the cross section σ_k does depend on $\hbar$, and the classical limit should correspond to $pR \gg \hbar$, $kR \gg 1$. However, the classical limit fails because there is an important difference between the classical calculation and quantum mechanical scattering. The classical calculation requires particles to hit the hard sphere with an impact parameter $b = |\boldsymbol{L}|/|\boldsymbol{p}|$ which is limited by the requirement that all scattered particles must actually hit the sphere, $b \leq R$. This corresponds to a classical angular momentum cutoff $|\boldsymbol{L}| \leq pR$. However, quantum mechanically, particles with arbitrary high angular momentum still feel the presence of the hard sphere and can be scattered similar to classical wave diffraction. This regime of deviation between the classical and quantum picture concerns large angular momenta and small deflection angles, i.e. the forward scattering region. In the classical picture the forward scattered particles are considered as missing the sphere and therefore ignored in the classical scattering cross section. Therefore the classical cross section is always smaller than the quantum mechanical cross section, even in the classical limit $kR \gg 1$. The increasing concentration of scattering in forward direction with increasing kR is demonstrated in Figures 11.3 and 11.4.

An approximate evaluation of the θ dependence of the extra "non-classical" part of the differential cross section for $kR \gg 1$ in terms of shadow forming

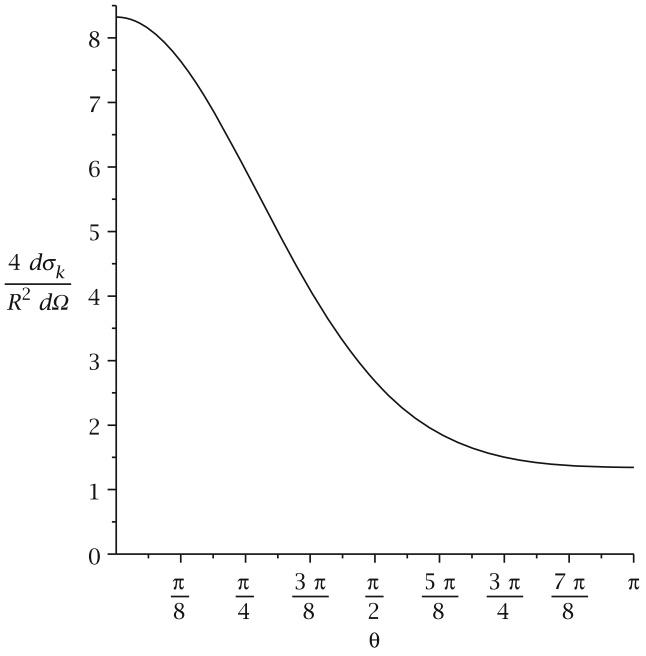


Figure 11.3: The differential scattering cross section $d\sigma_k/d\Omega$ of a hard sphere of radius R normalized to the classical differential scattering cross section $(d\sigma_k/d\Omega)_{classical} = R^2/4$ for $kR = 1$.

waves is given in [27]. However, the Figures 11.3 and 11.4 use the exact result (11.28). Either way, the ultimate reason for the discrepancy between the quantum result and the classical result in the classical limit $kR \gg 1$ is different accounting of scattered versus unscattered particles in the forward scattering region.

11.4 Rutherford scattering

Axial symmetry often plays a role in atoms which interact with their surroundings. External fields will often have axial symmetry, and this motivated Schrödinger to solve the hydrogen problem in parabolic coordinates for his perturbative analysis of the Stark effect[1]. Furthermore, if a hydrogen atom is formed through electron-proton recombination, the initial plane wave state describing the mutual approach of the electron and the proton will also break the rotational symmetry to axial symmetry and the calculation of recombination cross sections can be performed in terms of parabolic coordinates [2]. Maybe the best known application of parabolic coordinates concerns the calculation

[1] E. Schrödinger, Annalen Phys. 385, 437 (1926).

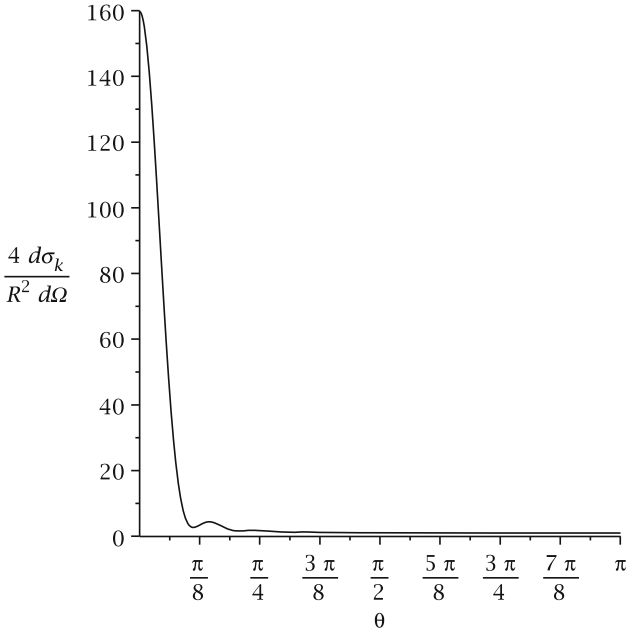


Figure 11.4: The differential scattering cross section $d\sigma_k/d\Omega$ of a hard sphere of radius R normalized to the classical differential scattering cross section $(d\sigma_k/d\Omega)_{classical} = R^2/4$ for $kR = 10$.

of Rutherford scattering. The incident plane wave $\psi^{(\mathrm{in})} \sim \exp(\mathrm{i}kz)$ breaks the rotational symmetry of the problem down to an axial symmetry, but we still expect an outgoing spherical wave $\psi^{(\mathrm{out})} \sim \exp(\mathrm{i}kr)/r$. The reconciliation of axial symmetry with the use of r makes parabolic coordinates more useful than cylinder coordinates for the study of scattering in rotationally symmetric potentials beyond the Born approximation, and can occasionally render them also more useful than spherical coordinates. The separability of the Coulomb problem in parabolic coordinates makes them particularly useful for the study of Rutherford scattering.
We define parabolic coordinates through the following relations[2],

$$x = 2\sqrt{\xi\eta}\cos\varphi, \quad y = 2\sqrt{\xi\eta}\sin\varphi, \quad z = \xi - \eta,$$

$$2\xi = r + z, \quad 2\eta = r - z, \quad \varphi = \arctan\frac{y}{x}. \tag{11.30}$$

Using the methods developed in Section 5.4, one finds the Schrödinger equation for motion of a particle of energy $E = \hbar^2k^2/2\mu$ in the Coulomb potential

[2]Please note that the definition used here differs by factors of 2 from the definition used by Schrödinger, $\lambda_1 \equiv \xi_S = 2\xi$, $\lambda_2 \equiv \eta_S = 2\eta$.

$V = q_1 q_2/4\pi\epsilon_0 r = \hbar^2 K/2\mu(\xi+\eta)$ in parabolic coordinates,

$$\frac{1}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right)+\frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right]\psi+\frac{1}{4\xi\eta}\frac{\partial^2\psi}{\partial^2\varphi}+k^2\psi-\frac{K}{\xi+\eta}\psi=0. \quad (11.31)$$

The arguments in Section 5.5, in particular concerning Hamiltonians of the form (5.34), imply that the solutions of this equation must have the form

$$\psi(\xi,\eta,\varphi) = f(\xi)g(\eta)\exp(\mathrm{i}m\varphi),$$

with the remaining separated equations

$$\left(\xi\frac{d}{d\xi}\right)^2 f+\left(k^2\xi^2-K_1\xi-\frac{m^2}{4}\right)f=0, \quad (11.32)$$

$$\left(\eta\frac{d}{d\eta}\right)^2 g+\left(k^2\eta^2-K_2\eta-\frac{m^2}{4}\right)g=0, \quad (11.33)$$

with $K_1+K_2=K$. We want $\psi^{(\mathrm{in})}\sim\exp(\mathrm{i}kz)=\exp(\mathrm{i}k\xi)\exp(-\mathrm{i}k\eta)$ to be the dominant term in the solution near the half-axis $z<0$, i.e. for $\xi\to 0$. This requirement complies with equation (11.32) if we choose $m=0$ and $K_1=\mathrm{i}k$. If we then substitute $f(\xi)=F(\xi)\exp(\mathrm{i}k\xi)$ into equation (11.32) to find the second solution, we find $F(\xi)=A+BE_i(-2\mathrm{i}k\xi)$, which implies a singularity of the second solution near the half-axis $z<0$. Therefore we conclude that the solution to our scattering problem must have the form $\psi(\xi,\eta)=g(\eta)\exp(\mathrm{i}k\xi)$ with the remaining condition

$$\eta\frac{d^2g}{d\eta^2}+\frac{dg}{d\eta}+\left(k^2\eta-K+\mathrm{i}k\right)g=0. \quad (11.34)$$

Comparison with equation (11.32) for $m=0$ and $K_1=\mathrm{i}k$ tells us that $g(\eta)=\exp(-\mathrm{i}k\eta)$ is the regular solution of equation (11.34) if $K=0$. This is also clear from the physical point of view. If there is no scattering potential, the plane wave $\exp(\mathrm{i}kz)=\exp(\mathrm{i}k\xi)\exp(-\mathrm{i}k\eta)$ that we imposed near the half-axis $z<0$ must persist everywhere. This motivates a substitution $g(\eta)=h(\eta)\exp(-\mathrm{i}k\eta)$ in (11.34),

$$\eta\frac{d^2h}{d\eta^2}+(1-2\mathrm{i}k\eta)\frac{dh}{d\eta}-Kh=0. \quad (11.35)$$

Substitution of $h(\eta)=\sum_{n\geq 0}c_n\eta^n$ yields

$$c_{n+1}=\frac{K+2\mathrm{i}kn}{(n+1)^2}c_n$$

and therefore

$$\begin{aligned} h(\eta) &= c_0\sum_{n=0}^{\infty}\frac{K(K+2\mathrm{i}k)\ldots(K+2\mathrm{i}k(n-1))}{n!}\frac{\eta^n}{n!} \\ &= c_0\,{}_1F_1(-\mathrm{i}K/2k;1;2\mathrm{i}k\eta)=c_0\exp(2\mathrm{i}k\eta)\,{}_1F_1(1+\mathrm{i}K/2k;1;2\mathrm{i}k\eta). \end{aligned}$$

The wave function for our scattering problem is therefore up to normalization[3]

$$\begin{aligned}\psi(\boldsymbol{r}) &= \exp[\mathrm{i}k(\xi-\eta)]_1F_1(-\mathrm{i}K/2k;1;2\mathrm{i}k\eta)\\ &= \exp(\mathrm{i}kz)_1F_1(-\mathrm{i}K/2k;1;\mathrm{i}k(r-z))\\ &= \exp(\mathrm{i}kr)_1F_1(1+\mathrm{i}K/2k;1;\mathrm{i}k(r-z)).\end{aligned} \tag{11.36}$$

The normalization factor c_0 is irrelevant because it cancels in the calculation of the cross section.

Identification of the incoming and scattered components in the wave function requires asymptotic expansion for large values of the argument $2k\eta = k(r-z)$. The asymptotic expansion of confluent hypergeometric functions ${}_1F_1(a;b;\zeta)$ for large $|\zeta|$ [1] yields the leading order terms

$$\begin{aligned}{}_1F_1(-\mathrm{i}K/2k;1;\mathrm{i}k(r-z)) \simeq \exp\left(\frac{\pi K}{4k}\right)\Bigg[&\frac{2k}{\mathrm{i}K}\Gamma^{-1}\left(\frac{\mathrm{i}K}{2k}\right)\\ &\times\exp\left(\frac{\mathrm{i}K}{2k}\ln[k(r-z)]\right)\left(1+\frac{K^2}{4\mathrm{i}k^3(r-z)}\right)\\ &+\frac{\exp[\mathrm{i}k(r-z)]}{\mathrm{i}k(r-z)}\Gamma^{-1}\left(\frac{K}{2\mathrm{i}k}\right)\\ &\times\exp\left(-\frac{\mathrm{i}K}{2k}\ln[k(r-z)]\right)\Bigg].\end{aligned}$$

After neglecting another irrelevant overall factor we find the asymptotic form

$$\begin{aligned}\psi(\boldsymbol{r}) &\simeq \exp\left(\mathrm{i}kz+\frac{\mathrm{i}K}{2k}\ln[k(r-z)]\right)\left(1+\frac{K^2}{4\mathrm{i}k^3r(1-\cos\theta)}\right)\\ &\quad+\frac{\Gamma(\mathrm{i}K/2k)}{\Gamma(-\mathrm{i}K/2k)}\frac{K}{2k^2r(1-\cos\theta)}\exp\left(\mathrm{i}kr-\frac{\mathrm{i}K}{2k}\ln[k(r-z)]\right)\\ &= \psi^{(\mathrm{in})}(\boldsymbol{r})+\psi^{(\mathrm{out})}(\boldsymbol{r}),\end{aligned} \tag{11.37}$$

where $\theta = \arccos(z/r)$ is the scattering angle.

This yields a differential scattering cross section

$$\frac{d\sigma}{d\Omega} = \lim_{r\to\infty}\frac{r^2 j_{out}}{j_{in}} = \left(\frac{K}{4k^2\sin^2(\theta/2)}\right)^2 = \left(\frac{q_1q_2}{16\pi\epsilon_0E}\right)^2\frac{1}{\sin^4(\theta/2)}, \tag{11.38}$$

which equals exactly the corresponding cross section calculated in classical mechanics and used by Rutherford in 1911 to infer the existence of a tiny positively charged nucleus in atoms. The cross section (11.38) is an example of a quantum mechanical result which is independent of $\hbar$ when expressed in terms of classical variables, and therefore it must agree with the classical result.

Use of the asymptotic expansion of the hypergeometric function ${}_1F_1(a;b;\zeta)$ for large $|\zeta|$ in the present case implies the requirement $kr(1-\cos\theta) =$

[3] W. Gordon, Z. Phys. 48, 180 (1928).

$2kr\sin^2(\theta/2) \gg 1$, i.e. the Rutherford formula is only applicable for scattering angles $\theta \gg \sqrt{2/kr} = \sqrt{\lambda/\pi r}$. This limitation is usually irrelevant, because the values of λ e.g. in the experiments of Geiger and Marsden were only a few femtometers.

11.5 Problems

11.1 The free time-dependent retarded Green's function in $\boldsymbol{x}$ representation has to satisfy the conditions

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\Delta\right)\mathcal{G}(\boldsymbol{x},t) = \delta(\boldsymbol{x})\delta(t), \quad \mathcal{G}(\boldsymbol{x},t)\Big|_{t<0} = 0.$$

Show that this function satisfies the following equations,

$$\begin{aligned}\mathcal{G}(\boldsymbol{x},t) &= \frac{1}{(2\pi)^4\hbar}\int d^3\boldsymbol{k}\int_{-\infty}^{\infty} d\omega\,\frac{\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)]}{\omega-(\hbar\boldsymbol{k}^2/2m)+\mathrm{i}\epsilon}\\ &= -\frac{m}{\pi\hbar^3}\int_{-\infty}^{\infty} dE\,G(\boldsymbol{x},E)\exp(-\mathrm{i}Et/\hbar)\\ &= \frac{\Theta(t)}{(2\pi)^3\mathrm{i}\hbar}\int d^3\boldsymbol{k}\,\exp\left[\mathrm{i}\left(\boldsymbol{k}\cdot\boldsymbol{x}-\frac{\hbar t}{2m}\boldsymbol{k}^2\right)\right]\\ &= \frac{\Theta(t)}{\mathrm{i}\hbar}\sqrt{\frac{m}{2\pi\mathrm{i}\hbar t}}^3\exp\left(\mathrm{i}\frac{m\boldsymbol{x}^2}{2\hbar t}\right). \end{aligned} \tag{11.39}$$

This also corresponds to the relation

$$\mathcal{G}(\boldsymbol{x},t) = \frac{\Theta(t)}{\mathrm{i}\hbar}U(\boldsymbol{x},t) = \frac{\Theta(t)}{\mathrm{i}\hbar}\langle\boldsymbol{x}|\exp\left(-\frac{\mathrm{i}t}{2m}\mathbf{p}^2\right)|0\rangle$$

between the retarded Green's function and the propagator for the free Schrödinger equation.

11.2 Calculate the differential scattering cross sections for the following potentials in Born approximation.
11.2a $V(r) = V_0\Theta(R-r)$,
11.2b $V(r) = V_0\exp(-r/R)$,
11.2c $V(r) = V_0\exp(-r^2/R^2)$.

11.3 Calculate the total cross sections for the potentials from problem **11.2** in Born approximation.

11.4 Calculate the differential cross section for Rutherford scattering in Born approximation. Compare with the exact result.

11.5 Calculate the differential cross section for Rutherford scattering with screened electromagnetic interactions in Born approximation. Use the following models for the screened interactions,
11.5a $V(r) = (qQ/4\pi\epsilon_0 r)\exp(-r/R)$,
11.5b $V(r) = (qQ/4\pi\epsilon_0 r)\exp(-r^2/R^2)$.

Chapter 12

The Density of States

Many applications of quantum mechanics require the concept of density of states. The notion of density of states is not entirely unique. Depending on the context and the requirements of the problem at hand, it most often refers to the number of quantum states per volume and per unit of energy, or to the number of states in a volume unit $d^3\boldsymbol{k}$ in $\boldsymbol{k}$ space, and for both notions there are several variants of the density of states. Therefore the purpose of this chapter is not only to introduce the concept of density of states, but also to enumerate all the different definitions which are commonly used in physics.

Various forms of the density of states appear in numerous places in physics, e.g. in thermodynamics and optics we need the density of photon states in the derivation of Planck's law, in solid state physics the density of electron states appears in the integral of energy dependent functions over the Brillouin zone, in statistical physics we need it to calculate energy densities in physical systems, and in quantum mechanics we need it to calculate transition probabilities involving states in an energy continuum, e.g. to calculate electron emission probabilities for ionization or for the photoelectric effect, or to calculate scattering cross sections. Transition probabilities involving quantum states in an energy continuum (e.g. unbound states or states in an energy band in a solid) involve the density of states per particle as the number of states dn per unit of volume in $\boldsymbol{k}$ space,

$$dn = d^3\boldsymbol{k}. \tag{12.1}$$

More precisely, this is a density of states per spin or polarization or helicity states of a particle. Otherwise it would have to be multiplied by the number g of spin or helicity states.

The densities of electron states, photon states, and all kinds of quasi-particle states in materials are also very important quantities in materials science. These densities determine the momentum and energy distributions of (quasi-)particles in materials, and the number of available states e.g. for charge or momentum transport, or for excitation of electrons or phonons. Densities of states therefore have profound impacts on electric and thermal conductivity and on optical properties of materials. We will see that there exist several

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ways to justify equation (12.1), and we will also explore the many different, but related definitions of the density of states.

12.1 Counting of oscillation modes

The basic notion of density of states concerns the $\boldsymbol{k}$ space density of linearly independent oscillation modes in a homogeneous volume. This is a very basic quantity in physics from which more advanced notions like local densities of states can be inferred. There are two basic ways to derive the $\boldsymbol{k}$ space density of states in a finite volume V. One of the derivations is more intuitive and the other one is slightly more formal, but the density of states is such an important concept that it is worthwhile to discuss both derivations.

The reasoning with periodic boundary conditions in a finite volume

The simplest derivation of (12.1) counts the number of independent oscillation modes in a rectangular cavity with periodic boundary conditions. A general wave vector can always be written in the form

$$\boldsymbol{k} = \frac{2\pi}{\lambda}\hat{\boldsymbol{k}} = \frac{2\pi}{\lambda}\sum_i \cos\theta_i\, \boldsymbol{e}_i,$$

where $\cos\theta_i$, $\sum_i \cos\theta_i^2 = 1$, are the directional cosines of the vector.

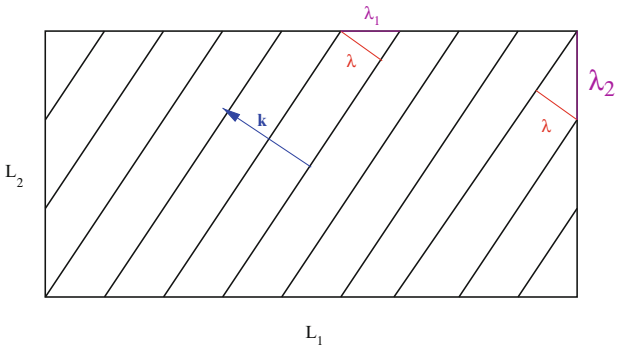


Figure 12.1: A standing wave in a cavity with periodic boundary conditions

Suppose that the wave has to be periodic with periodicity L_i in direction $\boldsymbol{e}_i$. In that case the length L_i must be an integer multiple of the projection $\lambda_i = \lambda/\cos\theta_i$ of the wavelength onto the direction $\boldsymbol{e}_i$:

$$L_i = n_i\lambda_i = n_i\frac{\lambda}{\cos\theta_i}, \quad n_i \geq 0, \tag{12.2}$$

see Figure 12.1.
Equation (12.2) can be written in terms of the components of the wave vector $\boldsymbol{k}$,

$$k_i = \frac{2\pi}{\lambda}\cos\theta_i = \frac{2\pi}{\lambda_i} = 2\pi\frac{n_i}{L_i}.$$

The volume of a single state in $\boldsymbol{k}$-space is therefore (with g spin or helicity states per wave)

$$\Delta^3\boldsymbol{k}\Big|_{\text{single state}} = \frac{(2\pi)^3}{gV},$$

since g helicity states reside in a cell of volume $(2\pi)^3/V$ in $\boldsymbol{k}$-space. This yields the proportionality factor between the measure for the number of states dn and the volume measure in $\boldsymbol{k}$-space,

$$dn = \frac{gV}{8\pi^3}d^3\boldsymbol{k}. \tag{12.3}$$

Inclusion of the factor g corresponds to a summation over all possible polarizations or helicities. This version of the density of states is often employed in thermodynamics and statistical physics. In quantum mechanics and scattering theory we often need the density of states with a given polarization or helicity,

$$dn = \frac{V}{8\pi^3}d^3\boldsymbol{k}. \tag{12.4}$$

We will mostly use the density (12.4) or its continuum limit, i.e. we will usually count states with a given polarization or helicity, e.g. states of spin up electrons, states of photons of given polarization, etc.

The reasoning based on the completeness of Fourier monomials

The Fourier monomials

$$\langle\boldsymbol{x}|\boldsymbol{n}\rangle = \frac{1}{\sqrt{V}}\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) = \frac{1}{\sqrt{V}}\exp\left(2\pi\mathrm{i}\sum_i\frac{n_i x_i}{L_i}\right) \tag{12.5}$$

provide a complete set of functions in a box of lengths L_i, cf. (10.2) and (10.3) for the one-dimensional versions of the following equations:

$$\frac{1}{V}\int_V d^3\boldsymbol{x}\,\exp\left(2\pi\mathrm{i}\sum_i\frac{n_i-n_i'}{L_i}x_i\right) = \delta_{\boldsymbol{n},\boldsymbol{n}'},$$

$$\frac{1}{V}\sum_{\boldsymbol{n}}\exp\left(2\pi\mathrm{i}\sum_i n_i\frac{x_i-x_i'}{L_i}\right) = \delta(\boldsymbol{x}-\boldsymbol{x}').$$

Therefore we find again $k_i = 2\pi n_i/L_i$ for the components of the $\boldsymbol{k}$ vectors, and the volume per base oscillation mode (with fixed polarization) is again

$$\Delta^3\boldsymbol{k}\Big|_{\text{single mode}} = \frac{8\pi^3}{V}.$$

This yields again the equation (12.4),

$$dn = \frac{V}{8\pi^3} d^3\boldsymbol{k}.$$

We remark that the measure dn for the number of states in $\boldsymbol{k}$-space (12.4) can also be written in terms of the wavenumbers $\tilde{\nu}_i \equiv 1/\lambda_i = k_i/2\pi$,

$$dn = \frac{V}{8\pi^3} d^3\boldsymbol{k} = V d^3\tilde{\boldsymbol{\nu}} = V d^3\frac{1}{\boldsymbol{\lambda}}.$$

If we also replace the volume V in position space with the volume measure $d^3\boldsymbol{x}$, we find a particularly intuitive and suggestive form for the corresponding measure of states in phase space,

$$dn = d^3\boldsymbol{x}\, d^3\tilde{\boldsymbol{\nu}} = d^3\boldsymbol{x}\, d^3\frac{1}{\boldsymbol{\lambda}} = \frac{d^3\boldsymbol{x}\, d^3\boldsymbol{p}}{h^3}.$$

Here $\boldsymbol{\lambda} = \lambda\hat{\boldsymbol{k}}$, and we define the "inverse" vector as $1/\boldsymbol{\lambda} \equiv \boldsymbol{\lambda}/\lambda^2$.

12.2 The continuum limit

In the limit $V \to \infty$, the discrete enumerable set of normalized plane waves in a cubic volume V, $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})/\sqrt{V}$, $\boldsymbol{k} = 2\pi\boldsymbol{n}/L = 2\pi\boldsymbol{n}/V^{1/3}$, is replaced by the continuous non-enumerable set $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})/\sqrt{2\pi}^3$. The easiest way to see this is through the completeness relation of the Fourier monomials in a cubic box and using $\Delta^3\boldsymbol{n} = 1$ for the volume of a triplet of integers in $\mathbb{Z}^3$,

$$\begin{aligned}
\delta(\boldsymbol{x}-\boldsymbol{x}') &= \frac{1}{V}\sum_{\boldsymbol{n}} \exp\left(\frac{2\pi\mathrm{i}}{V^{1/3}}\boldsymbol{n}\cdot(\boldsymbol{x}-\boldsymbol{x}')\right) \\
&= \frac{1}{V}\sum_{\boldsymbol{n}} \Delta^3\boldsymbol{n}\, \exp\left(\frac{2\pi\mathrm{i}}{V^{1/3}}\boldsymbol{n}\cdot(\boldsymbol{x}-\boldsymbol{x}')\right) \\
&= \frac{1}{V}\sum_{\boldsymbol{k}} \frac{V}{(2\pi)^3}\Delta^3\boldsymbol{k}\, \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')] \\
&\to \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\, \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]\,.
\end{aligned}$$

This corresponds to the substitution $V \Rightarrow (2\pi)^3$ in the plane waves, and the corresponding substitution for the measure for the number of states is indeed

$$dn = \frac{V}{(2\pi)^3} d^3\boldsymbol{k} \;\Rightarrow\; d^3\boldsymbol{k}. \tag{12.6}$$

Note that either way, the density of states per volume V of a particle with fixed helicity or spin is

$$\frac{dn}{V} = \frac{d^3\boldsymbol{k}}{(2\pi)^3}, \tag{12.7}$$

irrespective of whether we have taken the continuum limit or not. However, please also note that in the continuum limit both the differential number of states $dn = d^3\boldsymbol{k}$ and the number of states per volume $dn/V = d^3\boldsymbol{k}/(2\pi)^3$ come with dimensions length^{-3}. We have to keep this in mind when we are using dimensional analysis of quantum mechanical transition amplitudes in time-dependent perturbation theory in Chapters 13 and 18.

Another reasoning for the continuum limit

We consider the matrix element of the time evolution operator $U_D(t,t')$ between a bound hydrogen state $|n,\ell,m_\ell\rangle$ and a plane wave $|\boldsymbol{k}\rangle$. The motivation for considering matrix elements of U_D will be given in the following chapter. Unitarity of $U_D(t,t')$ and the completeness relation for plane waves imply

$$\int d^3\boldsymbol{k}\,|\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m_\ell\rangle|^2 = 1.$$

This tells us that we can interprete $|\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m_\ell\rangle|^2$ as a probability density for the system to end up in a plane wave state $|\boldsymbol{k}\rangle$, and $d^3\boldsymbol{k}$ as a measure for the number of states, such that the probability for the system to end up in a region $\mathcal{K}$ in $\boldsymbol{k}$ space is

$$P_{n,\ell,m_\ell\to\mathcal{K}}(t,t') = \int_{\mathcal{K}} d^3\boldsymbol{k}\,|\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m_\ell\rangle|^2.$$

This confirms yet again that $dn = d^3\boldsymbol{k}$ is the correct density of states in $\boldsymbol{k}$ space in the continuuum limit

Different forms of the density of states in a homogeneous medium

We may or may not include the number g of helicity or spin states in the density of states; we can normalize to finite volume V or take the continuum limit $V\to\infty$, and we may also use the density of states per $\boldsymbol{k}$ space volume and per direct volume V (i.e. normalize dn by V). All these simple alternatives amount to eight basic options for the density of states in $\boldsymbol{k}$ space,

$$dn = [g]\left[\frac{[V]}{8\pi^3}\right] d^3\boldsymbol{k}.$$

The first term in square brackets is included if we sum over all possible polarizations of the particle, and the fraction $V/(8\pi^3)$ is included if we use box normalization. The volume factor is not included if the density of states is also counted per volume in position space, dn/V. The fraction $V/(8\pi^3)$ in dn disappears in the continuum limit.

12.3 Density of states per unit of energy

In solid state physics (and in variants of time-dependent perturbation theory and scattering theory) one is often interested in transforming $d^3\boldsymbol{k}$ to variables $d^2\boldsymbol{k}_\parallel$ parallel to surfaces of constant energy $E(\boldsymbol{k})$ in $\boldsymbol{k}$ space and the energy E, which increases orthogonal to the surfaces of constant energy. The normalized unit vector in the direction of increasing E is

$$\hat{\boldsymbol{k}}_\perp = \frac{\partial E(\boldsymbol{k})/\partial \boldsymbol{k}}{|\partial E(\boldsymbol{k})/\partial \boldsymbol{k}|} = \frac{\boldsymbol{v}(\boldsymbol{k})}{|\boldsymbol{v}(\boldsymbol{k})|}$$

(recall that $\boldsymbol{v}(\boldsymbol{k}) = \hbar^{-1}\partial E(\boldsymbol{k})/\partial \boldsymbol{k}$ is the group velocity). Therefore we have

$$dk_\perp = d\boldsymbol{k}\cdot\hat{\boldsymbol{k}}_\perp = \frac{d\boldsymbol{k}\cdot\partial E(\boldsymbol{k})/\partial \boldsymbol{k}}{|\partial E(\boldsymbol{k})/\partial \boldsymbol{k}|} = \frac{dE}{|\partial E(\boldsymbol{k})/\partial \boldsymbol{k}|} = \frac{dE}{\hbar|\boldsymbol{v}(\boldsymbol{k})|}$$

and

$$d^3\boldsymbol{k} = d^2\boldsymbol{k}_\parallel \frac{dE}{|\partial E(\boldsymbol{k})/\partial \boldsymbol{k}|}.$$

Here $d^2\boldsymbol{k}_\parallel$ is some appropriate measure for coordinates along the constant energy surfaces.
An isotropic dispersion relation, $E(\boldsymbol{k}) = E(k)$, yields

$$d^3\boldsymbol{k} = d^2\Omega_{\boldsymbol{k}} k^2 \frac{dE}{dE/dk}.$$

The corresponding density number of states is then

$$dn = [g]\left[\frac{[V]}{8\pi^3}\right] d^2\Omega_{\boldsymbol{k}} k^2 \frac{dE}{|dE/dk|} = \varrho(E) dE d^2\Omega_{\boldsymbol{k}}, \tag{12.8}$$

with a density of states *per energy* or density of states *in the energy scale*

$$\varrho(E) = [g]\left[\frac{[V]}{8\pi^3}\right] k^2 \frac{dE}{|dE/dk|}. \tag{12.9}$$

Here the absolute value $|dE/dk|$ is taken in the denominator, because in cases where $dE/dk < 0$, the convention is to substitute an integral in positive dk direction with an integral in positive dE direction in the summation over states,

$$dk = \frac{dE}{dE/dk} \to \frac{dE}{|dE/dk|}.$$

In isotropic problems the angular variables are often integrated over, and one uses the convention

$$dn \to \varrho(E) dE$$

with the factor 4π included in ϱ. Altogether this leaves us with the following sixteen possibilities for the density of states in the energy scale,

$$\varrho(E) = [g]\left[\frac{[V]}{8\pi^3}\right][4\pi]\,\frac{k^2}{|dE/dk|}. \tag{12.10}$$

We remark that generalization of the previous arguments to d spatial dimensions yields the following results for the density of states,

$$dn = [g]\left[\frac{[V]}{(2\pi)^d}\right]d^d\boldsymbol{k}, \quad \varrho_d(E) = [g]\left[\frac{[V]}{(2\pi)^d}\right]\left[\frac{2\sqrt{\pi}^d}{\Gamma(d/2)}\right]\frac{k^{d-1}}{|dE/dk|}, \tag{12.11}$$

where $S_{d-1} = 2\sqrt{\pi}^d/\Gamma(d/2)$ is the $(d-1)$-dimensional hyper-area of a unit sphere in d dimensions. For the free non-relativistic particle in d dimensions we find in particular the following forms of the density of states in the energy scale,

$$\varrho_d(E) = \Theta(E)\,[g]\left[\frac{[V]}{(2\pi)^d}\right]\left[\frac{2\sqrt{\pi}^d}{\Gamma(d/2)}\right]\left(\frac{\sqrt{m}}{\hbar}\right)^d\sqrt{2E}^{d-2}.$$

The most commonly used version gives the density of free non-relativistic states per volume and per energy in d dimensions as

$$\varrho_d(E) = g\Theta(E)\sqrt{\frac{m}{2\pi}}^d\,\frac{\sqrt{E}^{d-2}}{\Gamma(d/2)\hbar^d}. \tag{12.12}$$

This simple formula is often employed for $d = 1$ and $d = 2$ to estimate the density of states in quantum wires or quantum wells. For $d = 3$ it yields the density of states in a free electron model for metals.

12.4 Density of states in radiation

The energy of a photon of frequency f is $E = hf = \hbar ck$ and we have $g = 2$ independent polarization states. Equations (12.3) or (12.10) therefore yield the following expressions for the density of photon states per volume and per unit of energy,

$$\varrho(E) = \frac{dn}{V\,dE} = \frac{2}{8\pi^3}4\pi k^2\frac{dk}{dE} = \frac{E^2}{\pi^2(\hbar c)^3},$$

or in d dimensions,

$$\varrho_d(E) = \frac{E^{d-1}}{2^{d-2}\pi^{d/2}\Gamma(d/2)(\hbar c)^d}.$$

The density of photon states (per volume V) in the frequency scale follows as

$$g_d(f) \equiv \varrho_d(f) = \frac{dn}{V\,df} = \frac{4\pi^{d/2}}{\Gamma(d/2)}\frac{f^{d-1}}{c^d}.$$

For $d = 3$ this is equation (1.6) which we have used in the derivation of Planck's law.

The density of states for other quantum systems

It is also useful to note that we can express the density of states per volume in plane waves trivially through the corresponding wave functions,

$$\frac{dn}{V} = \frac{d^3\boldsymbol{k}}{(2\pi)^3} = d^3\boldsymbol{k}\,|\langle \boldsymbol{x}|\boldsymbol{k}\rangle|^2\,.$$

This suggests the following identification of the number of states per volume in terms of quantum states which are labeled through a set of quantum numbers α,

$$\frac{dn}{V}(\boldsymbol{x}) = d\alpha\,|\langle \boldsymbol{x}|\alpha\rangle|^2\,. \tag{12.13}$$

From this observation we can infer a generalization of the density of states per volume and per unit of energy which also holds for discrete spectra. Suppose the Hamiltonian H has a discrete spectrum E_n and continuous spectra in ranges $E_{b1} \le E \le E_{b2}$. We use $\alpha = (E, \nu)$ for the set of quantum numbers, where ν is a set of degeneracy indices. Then the previous identification yields the density of states per volume and per energy as

$$\begin{aligned}\varrho(E,\boldsymbol{x}) = &\sum_n \delta(E-E_n) \sum\!\!\!\!\!\!\int d\nu_n\,|\langle \boldsymbol{x}|E_n,\nu_n\rangle|^2 \\ &+\sum_b \Theta(E-E_{b1})\Theta(E_{b2}-E) \sum\!\!\!\!\!\!\int d\nu(E)\,|\langle \boldsymbol{x}|E,\nu(E)\rangle|^2\,. \end{aligned}\tag{12.14}$$

E.g. the density of states per volume and per energy for the hydrogen atom would be (with factors of 2 from summation over spins)

$$\begin{aligned}\varrho(E,\boldsymbol{x}) = &\,2\sum_{n=1}^{\infty}\delta(E-E_n)\sum_{\ell=0}^{n-1}\sum_{m_\ell=-\ell}^{\ell}|\langle \boldsymbol{x}|n,\ell,m_\ell\rangle|^2 \\ &+\Theta(E)\sum_{\ell=0}^{\infty}\sum_{m_\ell=-\ell}^{\ell}\frac{1}{\hbar^3}\sqrt{(2m)^3E}\,|\langle \boldsymbol{x}|k,\ell,m_\ell\rangle|^2\,, \end{aligned}\tag{12.15}$$

where $\langle \boldsymbol{x}|k,\ell,m_\ell\rangle$ are the Coulomb waves $\psi_{k,\ell,m_\ell}(\boldsymbol{x})$ from Section 7.10 and $\sqrt{(2m)^3E}/\hbar^3 = 2k^2dk/dE$.
A short hand version of equation (12.14) is

$$\varrho(E,\boldsymbol{x}) = \sum\!\!\!\!\!\!\int dE'\,d\nu(E')\,\delta(E-E')\,|\langle \boldsymbol{x}|E',\nu(E')\rangle|^2\,. \tag{12.16}$$

Note that for each quantum system, the total number of single-particle states per volume diverges in a very specific way,

$$\int \frac{dn}{V} = g\langle \boldsymbol{x}|\boldsymbol{x}\rangle = g\delta(\boldsymbol{0}).$$

12.5 Problems

12.1 We consider a free gas of spin 1/2 fermions in a finite volume $V = L^3$ with periodic boundary conditions. This implies the constraints

$$k_i = \frac{2\pi}{L} n_i, \quad n_i \in \mathbb{Z}$$

on the components of the wave vector.
Our fermion gas contains $N \gg 1$ particles, and we assume it to be in the state of minimal energy. How large is the maximal momentum $p_F = \hbar k_F$ (the *Fermi momentum*) in the fermi gas?
You have to take into account that only two fermions can have the same momentum.

Solution

With $N \gg 1$ we have $\lambda_F \ll L$ or $k_F \gg \frac{2\pi}{L}$. The number of states with momenta $p \leq p_F$ is then

$$2\frac{4\pi}{3} k_F^3 \frac{L^3}{8\pi^3} = \frac{1}{3\pi^2} k_F^3 L^3 = N,$$

and therefore

$$k_F = \frac{1}{L} \left(3\pi^2 N\right)^{\frac{1}{3}} = \left(3\pi^2 n\right)^{\frac{1}{3}}, \quad p_F = \hbar k_F, \tag{12.17}$$

where $n = N/V$ is the particle density.

12.2 The equation (12.11) for the density of states in d dimensions holds for isotropic dispersion relations $E = E(|\boldsymbol{k}|)$. We used $k \equiv |\boldsymbol{k}|$ in (12.11).
For one-dimensional models that equation yields the density of states in the energy scale per volume $V \equiv a$ (a lattice constant) and per helicity state as

$$\varrho_1(E) = \frac{1}{ag} \frac{dn}{dE} = \frac{1}{2\pi} \times 2 \times \left| \frac{d|k|}{dE} \right|. \tag{12.18}$$

The factor of 2 comes from the "volume" $S_0 = [2\sqrt{\pi}^d / \Gamma(d/2)]_{d=1}$ of the zero-dimensional unit sphere. This sphere consists of the two points 1 and -1. Is equation (12.18) correct? Or should we abandon the factor of 2?

12.3 Equation (12.13) for the local density of states yields for one-dimensional lattices with volume $V = a$ and Bloch states (10.5) the local density of states in the k scale as

$$\varrho(k, x) = \frac{dn}{agdk}(x) = \sum_n |\psi_n(k, x)|^2.$$

Note that we also divided out the number g of spin or helicity states, which is included as a discrete parameter in the set of quantum numbers α in (12.13).

Show that transformation to the energy scale and spatial averaging reproduces the isotropic result (12.18),

$$\varrho(E) = \frac{1}{a}\int_0^a dx\, \varrho(E,x) = \frac{1}{\pi}\left|\frac{d|k|}{dE}\right| .$$

12.4 We consider the Kronig-Penney model from Section 10.4.
Show for $E > 0$ that the spatially averaged one-dimensional density of states in the energy scale,

$$\varrho(E) = \frac{dn}{agdE} = \frac{1}{\pi}\left|\frac{d|k|}{dE}\right| ,$$

is given by

$$\varrho(E) = \frac{m}{\pi\hbar^2 K}\left|\left(1+\frac{u}{(Ka)^2}\right)\sin(Ka) - \frac{u}{Ka}\cos(Ka)\right| \times \left[\left(1-\frac{u^2}{(Ka)^2}\right)\sin^2(Ka) - \frac{u}{Ka}\sin(2Ka)\right]^{-1/2} , \tag{12.19}$$

with $K = \sqrt{2mE}/\hbar$. This equation only applies where states exist, i.e. where the condition (10.30) is met. The resulting density of states for $u = 5$ in the region of the first two energy bands is plotted in Fig. 12.2 for a lattice constant $a = 3.5$ Å.

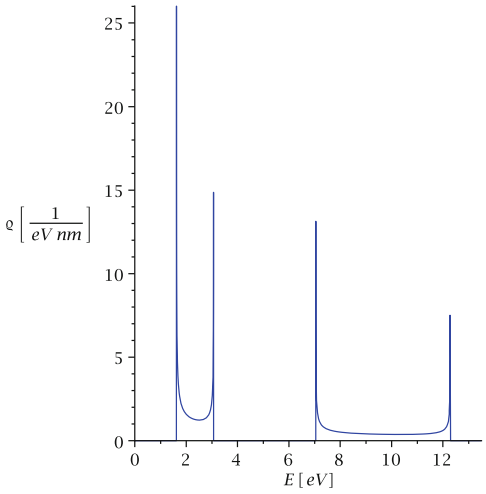


Figure 12.2: The one-dimensional density of states in the energy scale (12.19) for $u = 5$ and a lattice constant $a = 3.5$ Å. The energy scale covers the first two energy bands $E_0(k)$ and $E_1(k)$, cf. Fig. 10.2.

Chapter 13

Time-dependent Perturbations in Quantum Mechanics

The development of time-dependent perturbation theory was initiated by Paul Dirac's early work on the semi-classical description of atoms interacting with electromagnetic fields[1]. Dirac, Wheeler, Heisenberg, Feynman and Dyson developed it into a powerful set of techniques for studying interactions and time evolution in quantum mechanical systems which cannot be solved exactly. It is used for the quantitative description of phenomena as diverse as proton-proton scattering, photo-ionization of materials, scattering of electrons off lattice defects in a conductor, scattering of neutrons off nuclei, electric susceptibilities of materials, neutron absorption cross sections in a nuclear reactor etc. The list is infinitely long. Time-dependent perturbation theory is an extremely important tool for calculating properties of any physical system.
So far all the Hamiltonians which we had studied were time-independent. This property was particularly important for the time-energy Fourier transformation from the time-dependent Schrödinger equation to a time-independent Schrödinger equation. Time-independence of H also ensures conservation of energy, as will be discussed in detail in Chapter 16. Time-dependent perturbation theory, on the other hand, is naturally also concerned with time-dependent Hamiltonians $H(t)$ (although it provides very useful results also for time-independent Hamiltonians, and we will see later that most of its applications in quantum field theory concern sytems with time-independent Hamiltonians). We will therefore formulate all results in this chapter for time-dependent Hamiltonians, and only specify to time-independent cases where it is particularly useful for applications.

13.1 Pictures of quantum dynamics

As a preparation for the discussion of time-dependent perturbation theory (and of field quantization later on), we now enter the discussion of different *pictures*

[1] P.A.M. Dirac, Proc. Roy. Soc. London A 112, 661 (1926).

R. Dick, *Advanced Quantum Mechanics: Materials and Photons*,
Graduate Texts in Physics, DOI 10.1007/978-1-4419-8077-9_13,
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of quantum dynamics.
The picture which we have used so far is the *Schrödinger picture* of quantum dynamics: the time evolution of a system is encoded in its states $|\psi(t)\rangle$ which have to satisfy a Schrödinger equation $\mathrm{i}\hbar d|\psi_S(t)\rangle/dt = H(t)|\psi_S(t)\rangle$. However, every unitary transformation on states and operators $|\psi\rangle \to U|\psi\rangle$, $A \to U \cdot A \cdot U^+$ with a unitary operator U leaves the matrix elements $\langle\phi|A|\psi\rangle$ and therefore the observables of a system invariant.
If U is in particular a time-dependent unitary operator, then this changes the time-evolution of the states and operators without changing the time-evolution of the observables. Application of a time-dependent $U(t)$ corresponds to a change of the picture of quantum dynamics, and two important cases besides the Schrödinger picture are the *Heisenberg picture* and the *interaction (or Dirac) picture*. In the Heisenberg picture all time dependence is cast from the states onto the operators, whereas in the Dirac picture the operators follow a "free" (or better: exactly solvable) time evolution, while the interaction (non-solvable) part of the Hamiltonian determines the time evolution of the states. There are essentially two reasons for introducing the Heisenberg picture. The less important of these reasons is that the Hamilton-Poisson formulation of the classical limit of quantum systems is related to the Heisenberg picture. The really important reason is that quantum field theory in Chapter 17 appears first in the Heisenberg picture.
The rationale for introducing the Dirac picture is that time-dependent perturbation theory automatically leads to the calculation of matrix elements of the time evolution operator in the Dirac picture. As soon as we want to calculate transition probabilities in a quantum system under the influence of time-dependent perturbations, we automatically encounter the Dirac picture. Before immersing ourselves into the discussion of the Heisenberg and Dirac pictures, we have to take a closer look at time evolution in the Schrödinger picture.

Time evolution in the Schrödinger picture

In the Schrödinger picture the basic operators Φ_S (like $\mathbf{x}$ or $\mathbf{p}$) are time-independent, $d\Phi_S/dt = 0$, and all the time evolution from the dynamics is carried by the states. The differential equation

$$\mathrm{i}\hbar\frac{d}{dt}|\psi_S(t)\rangle = H(t)|\psi_S(t)\rangle$$

yields an equivalent integral equation

$$|\psi_S(t)\rangle = |\psi_S(t_0)\rangle - \frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)|\psi_S(\tau)\rangle,$$

and iteration of this equation yields

$$|\psi_S(t)\rangle = U(t,t_0)|\psi_S(t_0)\rangle$$

with the *time evolution operator*[2]

$$\begin{aligned} U(t,t_0) &= \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)\right) \\ &= \sum_n \frac{1}{(\mathrm{i}\hbar)^n}\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \ldots \int_{t_0}^{\tau_{n-1}} d\tau_n\, H(\tau_1)H(\tau_2)\ldots H(\tau_n) \\ &= \sum_n \frac{1}{(\mathrm{i}\hbar)^n}\int_{t_0}^{t} d\tau_n \int_{\tau_n}^{t} d\tau_{n-1} \ldots \int_{\tau_2}^{t} d\tau_1\, H(\tau_1)H(\tau_2)\ldots H(\tau_n). \end{aligned} \tag{13.1}$$

Taking the adjoint switches t with t_0 in the argument of the time evolution operator,

$$\begin{aligned} U^+(t,t_0) &= \sum_n \left(\frac{\mathrm{i}}{\hbar}\right)^n \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \ldots \int_{t_0}^{\tau_{n-1}} d\tau_n\, H(\tau_n)H(\tau_{n-1})\ldots H(\tau_1) \\ &= \sum_n \frac{1}{(\mathrm{i}\hbar)^n}\int_{t}^{t_0} d\tau_n \int_{t}^{\tau_n} d\tau_{n-1} \ldots \int_{t}^{\tau_2} d\tau_1\, H(\tau_n)H(\tau_{n-1})\ldots H(\tau_1) \\ &= \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t}^{t_0} d\tau\, H(\tau)\right) = U(t_0,t). \end{aligned} \tag{13.2}$$

This and the composition law (13.5) below imply unitarity of the time evolution operator.

Please note that the *time ordering operator* T always ensures that the Hamiltonians are ordered from right to left such that their time arguments go from closer to the *lower integration boundary* (t_0 in equation (13.1), t in equation (13.2)) to the *upper integration boundary* (t in equation (13.1), t_0 in equation (13.2)), *no matter whether the upper integration boundary is larger or smaller than the lower integration boundary*, e.g. if $t > t_0$ in equation (13.1) then of course $t_0 < t$ in equation (13.6). Apparently, the identification of "lower" and "upper" integration boundary in the previous statement implies the convention that the integrand in the exponent is $-\mathrm{i}H(t)/\hbar$. Otherwise the statement would be ambiguous.

The re-ordering of integrations in equations (13.1,13.2) is trivial for the 0th and 1st order terms. For the higher order terms e.g. in equation (13.1) we can recursively use for any consecutive pair of integrations

$$\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2\, A(\tau_1,\tau_2) = \int_{t_0}^{t} d\tau_2 \int_{\tau_2}^{t} d\tau_1\, A(\tau_1,\tau_2), \tag{13.3}$$

which proves the re-ordering for $n = 2$, see also Figure 13.1. For higher n we can perform an induction step,

$$\int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \ldots \int_{t_0}^{\tau_{n-1}} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n+1}\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1})$$

[2] F.J. Dyson, Phys. Rev. 75, 1736 (1949).

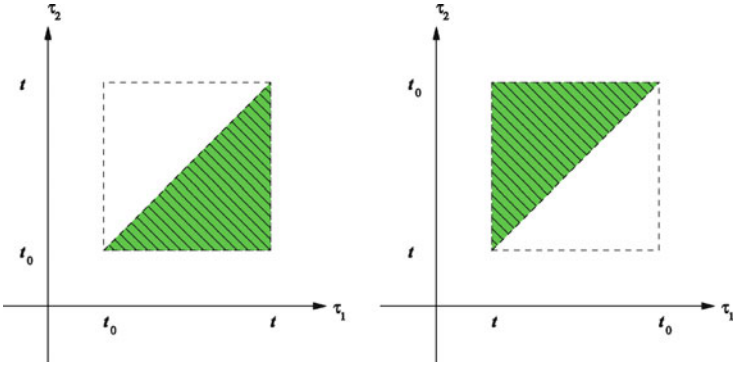


Figure 13.1: The integration domain in equation (13.3) is shown in green. The left panel is for $t > t_0$ (forward evolution by $U(t, t_0)$), the right panel is for $t < t_0$ (backward evolution by $U(t, t_0)$). In either case re-arranging of the order of integration over the same domain yields equation (13.3).

$$
\begin{aligned}
&= \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_{n+1} \int_{\tau_{n+1}}^{\tau_1} d\tau_n \ldots \int_{\tau_3}^{\tau_1} d\tau_2\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1}) \\
&= \int_{t_0}^{t} d\tau_{n+1} \int_{\tau_{n+1}}^{t} d\tau_1 \int_{\tau_{n+1}}^{\tau_1} d\tau_n \ldots \int_{\tau_3}^{\tau_1} d\tau_2\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1}) \\
&= \int_{t_0}^{t} d\tau_{n+1} \int_{\tau_{n+1}}^{t} d\tau_n \int_{\tau_n}^{t} d\tau_1 \int_{\tau_n}^{\tau_1} d\tau_{n-1} \ldots \int_{\tau_3}^{\tau_1} d\tau_2\, H(\tau_1)H(\tau_2)\ldots H(\tau_{n+1}) \\
&= \int_{t_0}^{t} d\tau_{n+1} \int_{\tau_{n+1}}^{t} d\tau_n \ldots \int_{\tau_3}^{t} d\tau_1 \int_{\tau_3}^{\tau_1} d\tau_2\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1}) \\
&= \int_{t_0}^{t} d\tau_{n+1} \int_{\tau_{n+1}}^{t} d\tau_n \ldots \int_{\tau_3}^{t} d\tau_2 \int_{\tau_2}^{t} d\tau_1\, H(\tau_1)H(\tau_2)\ldots H(\tau_n)H(\tau_{n+1}).
\end{aligned}
$$

The time derivatives yield

$$
\mathrm{i}\hbar\frac{\partial}{\partial t}U(t,t_0) = H(t)U(t,t_0), \quad \mathrm{i}\hbar\frac{\partial}{\partial t}U(t',t) = -U(t',t)H(t), \tag{13.4}
$$

$$
\mathrm{i}\hbar\frac{\partial}{\partial t}U^{+}(t,t_0) = -U^{+}(t,t_0)H(t),
$$

and the time evolution operator is the unique solution of these differential equations with initial condition $U(t_0, t_0) = 1$.
Another important property of the time evolution operator is the composition law

$$
U(t',t)U(t,t_0) = U(t',t_0). \tag{13.5}
$$

Proving this through multiplication of the left hand side and sorting out the nth order term is clumsy, due to the need to prove that the sum over $n + 1$

n-fold integrals on the left hand side really produces the nth order term on the right hand side. However, we can find a much more elegant proof by observing that $U(t',t)U(t,t_0)$ is actually independent of t due to equations (13.4),

$$\frac{\partial}{\partial t}U(t',t)U(t,t_0) = 0,$$

and therefore

$$U(t',t)U(t,t_0) = U(t',t')U(t',t_0) = U(t',t_0).$$

The composition law yields in particular

$$U(t_0,t)U(t,t_0) = U(t_0,t_0) = 1, \quad U(t_0,t) = U^{-1}(t,t_0),$$

and combined with (13.2) this implies unitarity of the time evolution operator,

$$U^{+}(t,t_0) = U(t_0,t) = U^{-1}(t,t_0). \tag{13.6}$$

The time evolution operator for the harmonic oscillator

The time evolution operator for time-independent Hamiltonians H is invariant under time translations,

$$U(t-t_0) = \exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t_0)\right).$$

The matrix elements in x space can then be written in terms of the wave functions of energy eigenstates $H|E,\nu\rangle = E|E,\nu\rangle$, where ν is a set of degeneracy indices. There are no degeneracy indices in one dimension and the expansion takes the form

$$\langle x|U(t)|x'\rangle = \sum\!\!\!\!\!\!\int dE\, \exp\left(-\frac{\mathrm{i}}{\hbar}Et\right)\langle x|E\rangle\langle E|x'\rangle.$$

E.g. the time evolution operator of the harmonic oscillator

$$U(t) = \exp\bigl(-\mathrm{i}\omega a^{+}at\bigr)\exp(-\mathrm{i}\omega t/2)$$

has matrix elements

$$\begin{aligned}\langle x|\exp\bigl(-\mathrm{i}\omega a^{+}at\bigr)|x'\rangle &= \sum_{n=0}^{\infty}\langle x|n\rangle\langle n|x'\rangle\exp(-\mathrm{i}n\omega t)\\ &= \sqrt{\frac{m\omega}{\pi\hbar}}\sum_{n=0}^{\infty}\frac{\exp(-\mathrm{i}n\omega t)}{2^n n!}H_n\left(\sqrt{\frac{m\omega}{\hbar}}x\right)\\ &\quad\times H_n\left(\sqrt{\frac{m\omega}{\hbar}}x'\right)\exp\left(-\frac{m\omega}{2\hbar}\left(x^2+x'^2\right)\right).\end{aligned}$$

Use of the Mehler formula (D.8) yields

$$\begin{aligned}\langle x|U(t)|x'\rangle &= \langle x|\exp\bigl(-\mathrm{i}\omega a^+ a t\bigr)\,|x'\rangle\exp(-\mathrm{i}\omega t/2)\\ &= \sqrt{\frac{m\omega}{2\pi\mathrm{i}\hbar\sin(\omega t)}}\exp\left(\mathrm{i}\frac{m\omega}{2\hbar}\frac{(x^2+x'^2)\cos(\omega t)-2xx'}{\sin(\omega t)}\right).\end{aligned}\tag{13.7}$$

To use the Mehler formula we should take $\omega\to\omega-\mathrm{i}\epsilon$ for $t>0$. This complies with the shifts $E'\to E'-\mathrm{i}\epsilon$,

$$\mathcal{G}(E)=\frac{1}{E-H+\mathrm{i}\epsilon}=\sum\!\!\!\!\!\!\int dE'\,\frac{|E'\rangle\langle E'|}{E-E'+\mathrm{i}\epsilon},$$

which define retarded Green's functions in the energy representation, see e.g. (11.6,20.14). The time-dependent retarded Green's function for the oscillator is related to the propagator (13.7) in the standard way

$$\langle x|\mathcal{G}(t)|x'\rangle=\frac{\Theta(t)}{\mathrm{i}\hbar}\langle x|U(t)|x'\rangle.$$

The Heisenberg picture

In the Heisenberg picture we use the unitary time evolution operator $U(t,t_0)$ to cast the time dependence from the states onto the operators,

$$|\psi_H\rangle=|\psi_S(t_0)\rangle=U^+(t,t_0)|\psi_S(t)\rangle,$$

$$\Phi_H(t)=U^+(t,t_0)\Phi_S U(t,t_0).$$

For the time evolution of the operators in the Heisenberg picture we observe that

$$\begin{aligned}\Phi_H(t)&=U^+(t,t_0)\Phi_S U(t,t_0)=U^+(t,t_0)\Phi_S U^+(t_0,t)\\ &=U^+(t,t')U^+(t',t_0)\Phi_S U^+(t_0,t')U^+(t',t)=U^+(t,t')\Phi_H(t')U(t,t'),\end{aligned}$$

and the Heisenberg evolution equation

$$\begin{aligned}\mathrm{i}\hbar\frac{d}{dt}\Phi_H(t)&=-U^+(t,t_0)[H(t)\Phi_S-\Phi_S H(t)]U(t,t_0)\\ &=-U^+(t,t_0)H(t)U(t,t_0)U^+(t,t_0)\Phi_S U(t,t_0)\\ &\quad+U^+(t,t_0)\Phi_S U(t,t_0)U^+(t,t_0)H(t)U(t,t_0)\\ &=-[H_H(t),\Phi_H(t)].\end{aligned}\tag{13.8}$$

In the last equation, $H_H(t)$ is the Hamiltonian written in terms of operators $\Phi_H(t)$ in the Heisenberg picture.
For time-dependent $\Phi_S(t)$ we have

$$\frac{d}{dt}\Phi_H(t)=U^+(t,t_0)\left(\frac{\mathrm{i}}{\hbar}[H(t),\Phi_S(t)]+\frac{d}{dt}\Phi_S(t)\right)U(t,t_0).$$

13.2 The Dirac picture

For the Dirac or interaction picture we split the Schrödinger picture Hamiltonian $H(t)$ into a "free" (or rather: solvable) part $H_0(t)$ and an "interaction" (or rather: perturbation) part $V(t)$,

$$H(t) = H_0(t) + V(t),$$

and define the "free" time evolution operator

$$U_0(t, t_0) = \mathrm{T} \exp\left(-\frac{\mathrm{i}}{\hbar} \int_{t_0}^{t} d\tau \, H_0(\tau) \right).$$

The common terminology of denoting $H_0(t)$ and $U_0(t, t_0)$ as "free" Hamiltonian and time evolution operator while $V(t)$ is the "interaction" part is motivated from scattering theory, which is one of the most common applications of time-dependent perturbation theory. However, we should always keep in mind that $H_0(t)$ does not really need to be a free particle Hamiltonian. E.g. for a hydrogen atom under the influence of an external electromagnetic field with wavelength $\lambda \gg a_0$, the "free" part H_0 would actually be the hydrogen Hamiltonian including the Coulomb interaction between the proton and the electron, while $V(t)$ would describe the effective coupling of the electromagnetic field to the quasi-particle which describes relative motion in the hydrogen atom. We will discuss this case in detail in Chapter 18, and in particular in Section 18.4.
The interaction picture splits off the solvable part of the time evolution from the states,

$$\begin{aligned} |\psi_D(t)\rangle &= U_0^+(t, t_0)|\psi_S(t)\rangle = U_0^+(t, t_0)U(t, t')|\psi_S(t')\rangle \\ &= U_0^+(t, t_0)U(t, t')U_0(t', t_0)|\psi_D(t')\rangle = U_D(t, t')|\psi_D(t')\rangle, \end{aligned} \tag{13.9}$$

where the last line identifies the time evolution operator $U_D(t, t')$ acting on the states in the interaction picture.
The solvable part of the time evolution is cast onto the operators

$$\begin{aligned} \Phi_D(t) &= U_0^+(t, t_0)\Phi_S U_0(t, t_0) = U_0^+(t, t_0)\Phi_S U_0^+(t_0, t) \\ &= U_0^+(t, t')U_0^+(t', t_0)\Phi_S U_0^+(t_0, t')U_0^+(t', t) \\ &= U_0^+(t, t')\Phi_D(t')U_0(t, t') \end{aligned} \tag{13.10}$$

to preserve the time evolution of matrix elements and expectation values in the interaction picture.
The differential equation for time evolution of the operators is

$$\begin{aligned} \mathrm{i}\hbar \frac{d}{dt}\Phi_D(t) &= -U_0^+(t, t_0)[H_0(t)\Phi_S - \Phi_S H_0(t)]U_0(t, t_0) \\ &= -U_0^+(t, t_0)H_0(t)U_0(t, t_0)U_0^+(t, t_0)\Phi_S U_0(t, t_0) \\ &\quad + U_0^+(t, t_0)\Phi_S U_0(t, t_0)U_0^+(t, t_0)H_0(t)U_0(t, t_0) \\ &= -[H_{0,D}(t), \Phi_D(t)], \end{aligned}$$

where in the last equation (similar to the previous remark for the Heisenberg picture) $H_{0,D}(t)$ is written in terms of operators $\Phi_D(t)$ in the Dirac picture. The interactions are encoded in the time evolution of the states,

$$\begin{aligned} \mathrm{i}\hbar\frac{d}{dt}|\psi_D(t)\rangle &= U_0^+(t,t_0)[H(t)-H_0(t)]|\psi_S(t)\rangle \\ &= U_0^+(t,t_0)[H(t)-H_0(t)]U_0(t,t_0)|\psi_D(t)\rangle \\ &= [H(t)-H_0(t)]_D|\psi_D(t)\rangle = H_D(t)|\psi_D(t)\rangle, \end{aligned} \tag{13.11}$$

where again $U_0^+(t,t_0)[H(t)-H_0(t)]U_0(t,t_0) = [H(t)-H_0(t)]_D$ due to the operator transition $\Phi_S \to \Phi_D$ in the Hamiltonians.
Conversion of equation (13.11) into the equivalent integral equation gives us another equation for the time evolution operator $U_D(t,t')$ for the states in the Dirac picture,

$$U_D(t,t') = U_0^+(t,t_0)U(t,t')U_0(t',t_0) = \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right). \tag{13.12}$$

This evolution operator apparently satisfies

$$\mathrm{i}\hbar\frac{\partial}{\partial t}U_D(t,t') = H_D(t)U_D(t,t').$$

We have split the time evolution unequally between states and operators, and therefore there are two Hamiltonians and related time evolution operators in the interaction picture: the "free" Hamiltonian $H_0(t)$ for the evolution of the operators and the interaction Hamiltonian $H_D(t)$ for the evolution of the states (and then there is the third Hamiltonian $H(t)$ and its time evolution operator appearing in the derivation of the interaction picture).
If we substitute[3]

$$H_D(t) = U_0^+(t,t_0)V(t)U_0(t,t_0) = U_0(t_0,t)V(t)U_0(t,t_0)$$

into equation (13.12) and use the composition property for time evolution operators

$$U_0(\tau,t_0)U_0(t_0,\tau') = U_0(\tau,\tau'),$$

we find

$$\begin{aligned} U_D(t,t') &= \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right) \\ &= \sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t} d\tau_1 \int_{t'}^{\tau_1} d\tau_2 \ldots \int_{t'}^{\tau_{n-1}} d\tau_n\, H_D(\tau_1)H_D(\tau_2)\ldots H_D(\tau_n) \\ &= \sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t} d\tau_1 \int_{t'}^{\tau_1} d\tau_2 \ldots \int_{t'}^{\tau_{n-1}} d\tau_n\, U_0(t_0,\tau_1)V(\tau_1)U_0(\tau_1,\tau_2) \\ &\quad \times V(\tau_2)U_0(\tau_2,\tau_3)\ldots U_0(\tau_{n-1},\tau_n)V(\tau_n)U_0(\tau_n,t_0). \end{aligned} \tag{13.13}$$

[3]The transformation law for operators from the Schrödinger picture into the interaction picture implies $H_D(t) \equiv V_D(t)$. The notation $V_D(t)$ is therefore also often used for $H_D(t)$.

The n-th term in the sum can be interpreted as n scatterings at the perturbation $V(t)$, with "free" time evolution under the Hamiltonian $H_0(t)$ between any two scattering events:

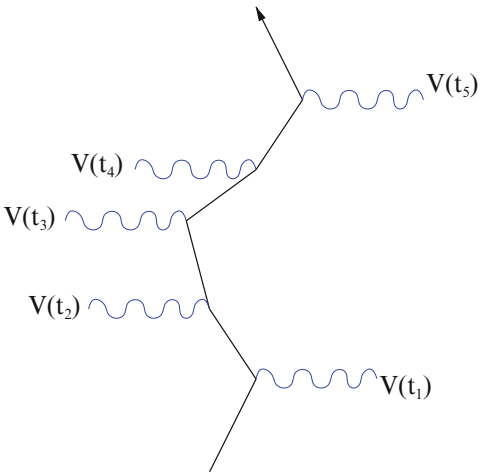


Figure 13.2: Scattering off a time-dependent perturbation.

and in the end everything is evolved again to the fiducial time t_0, see Figure 13.2.

Dirac picture for constant H_0

We have $H_0 = H_{0,D}$ if H_0 is a time-independent operator in the Schrödinger picture, because H_0 and $U_0(t, t_0) = \exp[-\mathrm{i}H_0(t - t_0)/\hbar]$ commute.

The Hamiltonian $H_D(t)$ acting on the states in the interaction picture is related to the Hamiltonian with the ordinary operators $\mathbf{p}$, $\mathbf{x}$,... of the Schrödinger picture via

$$H_D(t) = U_0^+(t, t_0)[H(t) - H_0(t)]U_0(t, t_0) = U_0^+(t, t_0)V(t)U_0(t, t_0).$$

This yields for time-independent H_0 in the Schrödinger picture:

$$H_D(t) = \exp\left(\frac{\mathrm{i}}{\hbar}H_0(t - t_0)\right) V(t) \exp\left(-\frac{\mathrm{i}}{\hbar}H_0(t - t_0)\right).$$

The time evolution operator for the states in the interaction picture is then

$$\begin{aligned} U_D(t,t') &= \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right) \\ &= \sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t} d\tau_1 \int_{t'}^{\tau_1} d\tau_2 \ldots \int_{t'}^{\tau_{n-1}} d\tau_n \exp\left(-\frac{\mathrm{i}}{\hbar}H_0(t_0-\tau_1)\right) \\ &\quad \times V(\tau_1)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_1-\tau_2)\right)V(\tau_2)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_2-\tau_3)\right)\ldots \\ &\quad \times \exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_{n-1}-\tau_n)\right)V(\tau_n)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_n-t_0)\right). \end{aligned} \tag{13.14}$$

The case of time-independent unperturbed operators H_0 is the most common case in applications of time-dependent perturbation theory. Equation (13.14) therefore shows the most commonly employed form of $U_D(t,t')$ for the evaluation of the transition amplitudes or scattering matrix elements which will be introduced in Section 13.3.

13.3 Transitions between discrete states

We are now in a position to discuss transitions in a quantum system under the influence of time-dependent perturbations. We are still operating in the framework of "ordinary" quantum mechanics ("first quantized theory"), and at this stage time-dependent perturbations of a quantum system arise from time dependence of the parameters in the Schrödinger equation.

We will denote states as *discrete states* if they can be characterized by a set of discrete quantum numbers, e.g. the bound energy eigenstates $|n,\ell,m_\ell,m_s\rangle$ of hydrogen or the states $|n_1,n_2,n_3\rangle$ of a three-dimensional harmonic oscillator are discrete. States which require at least one continuous quantum number for their labeling are denoted as *continuous states*. Momentum eigenstates $|\boldsymbol{k}\rangle$ are examples of continuous states. Quantum mechanical transitions involving continuous states require special considerations. Therefore we will first discuss transitions between discrete states, e.g. transitions between atomic or molecular bound states.

We consider a system with an unperturbed Hamiltonian H_0 under the influence of a perturbation $V(t)$:

$$H(t) = H_0 + V(t).$$

The perturbation operator will in general be a function of the operators $\mathbf{p}$ and $\mathbf{x}$, $V(t) \equiv V(\mathbf{p},\mathbf{x},t)$. We will see later that in many applications $V(t)$ has the form

$$V(\mathbf{p},\mathbf{x},t) = V_1(\mathbf{x},t) + \mathbf{p}\cdot\boldsymbol{V}_2(\mathbf{x},t). \tag{13.15}$$

In this section we assume that all states under consideration can be normalized to 1.

For the calculation of transition probabilities in the system, recall that the expansion of a general state $|\phi\rangle$ in terms of an orthonormal complete set of states $|\psi_n\rangle$ is

$$|\phi\rangle = \sum_n |\psi_n\rangle\langle\psi_n|\phi\rangle,$$

and therefore the probability of finding the state $|\psi_n\rangle$ in a measurement performed on the state $|\phi\rangle$ is $|\langle\psi_n|\phi\rangle|^2$.

Now assume that the state $|\phi\rangle$ is a state $|\psi_{in}(t)\rangle$, where the state at an earlier time $t' < t$ was an unperturbed state $|\psi_{in}^{(0)}(t')\rangle$, typically an eigenstate of H_0. Then we know that the state at time t is

$$|\psi_{in}(t)\rangle = U(t,t')|\psi_{in}^{(0)}(t')\rangle,$$

and since the state now evolved with the full Hamiltonian including the perturbation $V(t)$, it will not be an unperturbed state any more, but a superposition of unperturbed states. If at time t a measurement is performed on the state $|\psi_{in}(t)\rangle$, the probability to measure a certain unperturbed state $|\psi_{out}^{(0)}(t)\rangle$ will be $|\langle\psi_{out}^{(0)}(t)|\psi_{in}(t)\rangle|^2$.

Therefore the probability amplitude for transition from an unperturbed state $|\psi_{in}^{(0)}(t')\rangle$ to an unperturbed state $|\psi_{out}^{(0)}(t)\rangle$ between times t' and t is

$$\begin{aligned}\langle\psi_{out}^{(0)}(t)|\psi_{in}(t)\rangle &= \langle\psi_{out}^{(0)}(t)|U(t,t')|\psi_{in}^{(0)}(t')\rangle \\ &= \langle\psi_{out}^{(0)}(t_0)|U_0^+(t,t_0)U(t,t')U_0(t',t_0)|\psi_{in}^{(0)}(t_0)\rangle \\ &= \langle\psi_{out}^{(0)}(t_0)|U_D(t,t')|\psi_{in}^{(0)}(t_0)\rangle. \qquad (13.16)\end{aligned}$$

The transition probability amplitudes between unperturbed states are matrix elements of the time evolution operator in the interaction picture, where the unperturbed states are taken at some arbitrary fixed time.

The Schrödinger equations for the unperturbed states $|\psi^{(0)}(t_0)\rangle$ and the free evolution operators $U_0(t',t_0)$ and $U_0^+(t,t_0)$ imply

$$\frac{\partial}{\partial t_0}\langle\psi_{out}^{(0)}(t_0)|U_0^+(t,t_0)U(t,t')U_0(t',t_0)|\psi_{in}^{(0)}(t_0)\rangle = 0,$$

i.e. the choice of the parameter t_0 is (of course) irrelevant for the transition matrix element. We set $t_0 = 0$ in the following.

If we substitute the expansion (13.13) for the time evolution operator in the

interaction picture we get a series

$$\langle\psi^{(0)}_{out}(0)|U_D(t,t')|\psi^{(0)}_{in}(0)\rangle = \langle\psi^{(0)}_{out}(0)|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau H_D(\tau)\right)|\psi^{(0)}_{in}(0)\rangle$$
$$= \sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t}d\tau_1\int_{t'}^{\tau_1}d\tau_2\ldots\int_{t'}^{\tau_{n-1}}d\tau_n\,\langle\psi^{(0)}_{out}(0)|\exp\left(\frac{\mathrm{i}}{\hbar}H_0\tau_1\right)$$
$$\times V(\tau_1)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_1-\tau_2)\right)V(\tau_2)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_2-\tau_3)\right)$$
$$\times\ldots\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(\tau_{n-1}-\tau_n)\right)V(\tau_n)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0\tau_n\right)|\psi^{(0)}_{in}(0)\rangle. \quad (13.17)$$

Now we assume that our unperturbed states are energy eigenstates

$$|\psi^{(0)}_{out}(0)\rangle = |\psi_n(0)\rangle = |n\rangle, \qquad H_0|\psi_n(0)\rangle = E_n|\psi_n(0)\rangle,$$
$$|\psi^{(0)}_{in}(0)\rangle = |\psi_m(0)\rangle = |m\rangle, \qquad H_0|\psi_m(0)\rangle = E_m|\psi_m(0)\rangle$$

of the unperturbed Hamiltonian. Equation (13.17) then yields for the transition probability amplitude between eigenstates of H_0 (see also equation (13.14)),

$$\langle n|U_D(t,t')|m\rangle = \delta_{n,m} - \frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau\,\exp(\mathrm{i}\omega_{nm}\tau)\langle n|V(\tau)|m\rangle$$
$$-\frac{1}{\hbar^2}\sum_l\int_{t'}^{t}d\tau_1\int_{t'}^{\tau_1}d\tau_2\,\exp(\mathrm{i}\omega_{nl}\tau_1)\langle n|V(\tau_1)|l\rangle$$
$$\times\exp(\mathrm{i}\omega_{lm}\tau_2)\langle l|V(\tau_2)|m\rangle+\ldots, \quad (13.18)$$

with the transition frequencies $\omega_{nm} = (E_n - E_m)/\hbar$.
The transition probability from a discrete state $|m\rangle$ to a discrete state $|n\rangle$ is then

$$P_{m\to n}(t,t') = \left|\langle n|U_D(t,t')|m\rangle\right|^2. \quad (13.19)$$

Equation (13.18) assumes that we use eigenstates of H_0 for the initial and final states, but equation (13.19) holds for arbitrary discrete initial and final states, and we even do not have to require the same basis for the decomposition of the initial and the final state, i.e. equation (13.19) also holds if m and n are discrete quantum numbers referring to different bases of states.
$P_{m\to n}(t,t')$ is a dimensionless number if both the initial and final states are discrete states, i.e. dimensionless states (see the discussion of dimensions of states in Section 5.3), and due to the unitarity of $U_D(t,t')$ it is also properly normalized as a probability,

$$\sum_n P_{m\to n}(t,t') = \sum_n\langle m|U_D^+(t,t')|n\rangle\langle n|U_D(t,t')|m\rangle = \langle m|m\rangle = 1.$$

We will denote the *transition probability amplitude* $\langle n|U_D(t,t')|m\rangle$ also as a *scattering matrix element* or S *matrix element*,

$$\begin{aligned} S_{nm}(t,t') &= \langle n|U_D(t,t')|m\rangle = \langle n|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right)|m\rangle \\ &= \langle m|U_D^+(t,t')|n\rangle^* = \langle m|U_D(t',t)|n\rangle^* = \left(S^{-1}_{mn}(t,t')\right)^* \\ &= \left(S^{-1+}(t,t')\right)_{nm}. \end{aligned} \tag{13.20}$$

In the literature this definition is more commonly employed with default values $t\to\infty$, $t'\to-\infty$ for the initial and final times, $S_{nm}\equiv S_{nm}(\infty,-\infty)$. It is also usually reserved for transitions with two particles in the initial state (to be discussed in Chapter 17 and following chapters), but here we are still dealing with a single particle perturbed by a potential $V(t)$, or an effective single particle description of relative motion of two particles. The connection with many particle scattering theory later on is easier if we introduce the scattering matrix already for single particle problems, and it is also useful to have this notion available for arbitrary initial and final times.

Møller operators

At this point it is also interesting to note a factorized representation of the time evolution operator in the interaction picture, which is applicable if both H and H_0 do not depend on time. In this case we have with $t_0=0$,

$$U_D(t,t') = \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t'\right) = \Omega^+(t)\Omega(t')$$

with the Møller operator

$$\Omega(t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t\right).$$

Let us repeat the basic equation (13.16) and substitute this definition,

$$\begin{aligned} \langle\psi^{(0)}_{out}(t)|\psi_{in}(t)\rangle &= \langle\psi^{(0)}_{out}(t)|U(t,t')|\psi^{(0)}_{in}(t')\rangle = \langle\psi^{(0)}_{out}|U_0^+(t)U(t,t')U_0(t')|\psi^{(0)}_{in}\rangle \\ &= \langle\psi^{(0)}_{out}|U_D(t,t')|\psi^{(0)}_{in}\rangle = \langle\psi^{(0)}_{out}|\Omega^+(t)\Omega(t')|\psi^{(0)}_{in}\rangle \\ &= \langle\Psi_{out}\{t\}|\Psi_{in}\{t'\}\rangle. \end{aligned}$$

Here we have introduced states

$$\begin{aligned} |\Psi\{t\}\rangle = \Omega(t)|\psi^{(0)}\rangle &= \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t\right)|\psi^{(0)}\rangle \\ &= \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)|\psi^{(0)}(t)\rangle. \end{aligned}$$

For the interpretation of these states we notice

$$\exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right)|\Psi\{t\}\rangle = |\psi^{(0)}(t)\rangle,$$

i.e. $|\Psi\{t\}\rangle$ is the fictitious interacting state at time $t_0 = 0$ which yields the unperturbed state $|\psi^{(0)}(t)\rangle$ at time t under *full* time evolution from $t_0 = 0$ to t. In the framework or quantum mechanics, the case that both H and H_0 are time-independent would often be dealt with in the framework of time-independent perturbation theory or potential scattering theory. However, we will see later that in the framework of quantum field theory, time-independent H and H_0 is very common in applications of time-dependent perturbation theory.

First order transition probability between discrete energy eigenstates

For $n \neq m$, the first order result for S_{nm} is the matrix element of the Fourier component $V(\omega_{nm})$,

$$S_{nm} = -\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty} dt\, \exp(\mathrm{i}\omega_{nm}t)\langle n|V(t)|m\rangle = -\frac{\mathrm{i}}{\hbar}\sqrt{2\pi}\langle n|V(\omega_{nm})|m\rangle. \tag{13.21}$$

If the time dependence of the perturbation $V(t)$ is such that the Fourier transform $V(\omega)$ exists in the sense of standard Fourier theory (i.e. if $V(\omega)$ is a sufficiently well behaved function, which is the case e.g. if $V(t)$ is absolutely integrable or square integrable with respect to t), then the first order scattering matrix (13.21) provides us with finite first order approximations for transition probabilities

$$P_{m\to n} = |S_{nm}|^2 = \frac{2\pi}{\hbar^2}\left|\langle n|V(\omega_{nm})|m\rangle\right|^2. \tag{13.22}$$

Note that the Fourier transform

$$V(\omega) = \frac{1}{\sqrt{2\pi}}\int dt\, \exp(\mathrm{i}\omega t)V(t)$$

of a potential $V(t)$ has the dimension energy×time. Therefore $P_{m\to n}$ is a dimensionless number, as it should be. Furthermore, the probability interpretation and the use of first order perturbation theory entail that we should have $|\langle n|V(\omega_{nm})|m\rangle| < \hbar/\sqrt{2\pi}$.

The first order transition probability between discrete states requires existence of a regular Fourier tansform $V(\omega)$ of the perturbation $V(t)$. This condition is not satisfied in the important case of monochromatic perturbations like $V(t) = W\exp(-\mathrm{i}\omega t)$, which have a δ function as Fourier transform,

$$V(t) = W\exp(-\mathrm{i}\omega t), \quad V(\omega_{nm}) = \sqrt{2\pi}W\delta(\omega_{nm} - \omega).$$

Consistent treatment of this case requires that at least one of the states involved is part of a continuum of states, as discussed in Sections 13.4 and 13.5.

If both the initial and final atomic or molecular state are discrete, then the perturbation $V(t) = W\exp(-\mathrm{i}\omega t)$ must be treated as arising from a quantized field which comes with its own continuum of states. Monochromatic perturbations $V(t) = W\exp(\pm\mathrm{i}\omega t)$ typically arise from photon absorption or emission, and the previous statement simply means that the consistent treatment of transitions between bound states due to monochromatic perturbations requires the full quantum theory of the photon, see Section 18.5. See also problem 4 for an explanation why the Golden Rule, which is discussed in the next section, cannot be used for transitions between discrete states.

13.4 Transitions from discrete states into continuous states – ionization or decay rates

Ionization of atoms or molecules, transitions from discrete donor states into conduction bands in doped semiconductors, or disintegration of nuclei are processes where particles make a transition from discrete states into states in a continuum.

We assume that the unperturbed Hamiltonian H_0 contains an attractive radially symmetric potential which generates bound states $|n,\ell,m\rangle$, where ℓ and m are the usual angular momentum quantum numbers for the bound states and the quantum number n labels the energy levels. The free states for H_0 are usually given in terms of hypergeometric functions, e.g. the Coulomb waves $|k,\ell,m\rangle$ from Section 7.10.

Here we initially use plane wave states instead and ask what is the probability for the system to go from a bound state $|n,\ell,m\rangle$ into a plane wave state $|\boldsymbol{k}\rangle$ under the influence of a perturbation $V(t)$. This is a simplification, but the prize that we pay is that the transition matrix elements from a bound state into plane waves do not necessarily tell us something about ionization or decay of a bound system, because those transition matrix elements will also not vanish for perturbations which primarily generate another bound state. In that case they only tell us something about the generically non-vanishing Fourier coefficients of the new bound state. However, the focus in this preliminary discussion is not the calculation of actual ionization rates, but to explain how continuous final states affect the interpretation of transition matrix elements.

For continuous final states like $|\boldsymbol{k}\rangle$, the appropriate projection of $U_D(t,t')\,|\psi_{in}^{(0)}\rangle$ is onto the dimensionless combination $\sqrt{d^3\boldsymbol{k}}\langle\boldsymbol{k}|$. This means that in a transition from a discrete state $|n,\ell,m\rangle$ into a momentum eigenstate $\boldsymbol{k}$, the dimensionless quantity

$$\sqrt{d^3\boldsymbol{k}}\,S_{\boldsymbol{k};n,\ell,m}(t,t') = \sqrt{d^3\boldsymbol{k}}\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle$$

is a *differential transition probability amplitude*, in the sense that

$$dP_{n,\ell,m\to\boldsymbol{k}}(t,t') = d^3\boldsymbol{k}\,|\langle\boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle|^2$$

is a *differential transition probability* for the transition from the discrete state into a volume element $d^3\boldsymbol{k}$ around the vector $\boldsymbol{k}$ in momentum space. The meaning of this statement is that

$$P_{n,\ell,m\to\mathcal{K}}(t,t') = \int_{\mathcal{K}} d^3\boldsymbol{k}\, |\langle \boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle|^2 \tag{13.23}$$

is the *transition probability* from the discrete state $|n,\ell,m\rangle$ into a volume $\mathcal{K}$ in $\boldsymbol{k}$-space. Another way to say this is to denote the quantity with the dimension length^3

$$\mathcal{P}_{n,\ell,m\to\boldsymbol{k}}(t,t') = \frac{dP_{n,\ell,m\to\boldsymbol{k}}(t,t')}{d^3\boldsymbol{k}} = |\langle \boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle|^2$$

as the *transition probability density* per $\boldsymbol{k}$-space volume. The S matrix element

$$S_{\boldsymbol{k};n,\ell,m}(t,t') = \langle \boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle$$

is then a transition probability density amplitude.
With this interpretation, the transition amplitudes into continuous states yield correctly normalized probabilities, e.g. for plane waves,

$$\begin{aligned}\int d^3\boldsymbol{k}\, \mathcal{P}_{n,\ell,m\to\boldsymbol{k}}(t,t') &= \int d^3\boldsymbol{k}\, |\langle \boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle|^2 \\ &= \int d^3\boldsymbol{k}\, \langle n,\ell,m|U_D^+(t,t')|\boldsymbol{k}\rangle\langle \boldsymbol{k}|U_D(t,t')|n,\ell,m\rangle \\ &= \langle n,\ell,m|U_D^+(t,t')U_D(t,t')|n,\ell,m\rangle \\ &= \langle n,\ell,m|n,\ell,m\rangle = 1.\end{aligned}$$

The important conclusion from this is that transition matrix elements of $U_D(t,t')$ from discrete states into continuous final states yield transition probability *densities*, which have to be integrated to yield transition probabilities.

Ionization probabilities for hydrogen

Now that we have clarified the meaning of transition amplitudes from discrete into continuous states with the familiar basis of plane wave states, let us come back to the ionization or decay problems, i.e. transition from the discrete bound spectrum of an unperturbed Hamiltonian H_0 into the continuum of unbound states.
In particular, the unperturbed Hamiltonian for hydrogen is

$$H_0 = \frac{\mathbf{p}^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0|\mathbf{r}|} \tag{13.24}$$

and the ionization problem concerns transitions from bound states $|n,\ell,m\rangle$ into

Coulomb waves $|k,\ell,m\rangle$ under the influence of a time-dependent perturbation[4] $V(t)$. The contribution from Coulomb waves to the decomposition of unity in terms of hydrogen states came with a measure k^2dk (7.69), and therefore the probability for a transition $|n,\ell,m\rangle \to [k_1,k_2]$ into a momentum magnitude in the interval $[k_1,k_2]$ $(0 \le k_1 < k_2 < \infty)$ with fixed final state quantum numbers (ℓ',m') is

$$\begin{aligned} P_{n,\ell,m\to[k_1,k_2],\ell',m'} &= \int_{k_1}^{k_2} dk\, k^2\, |S_{k,\ell',m';n,\ell,m}|^2 \\ &= \int_{k_1}^{k_2} dk\, k^2\, |\langle k,\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2. \end{aligned}$$

If we want to know the probability for the hydrogen atom to ionize into a state with momentum magnitude $k_1 \le k \le k_2$ of the relative motion between proton and electron, we have to calculate

$$P_{n,\ell,m\to[k_1,k_2]} = \sum_{\ell'=0}^{\infty} \sum_{m'=-\ell'}^{\ell'} P_{n,\ell,m\to[k_1,k_2],\ell',m'}.$$

Note that the total ionization probability $P_{n,\ell,m} \equiv P_{n,\ell,m\to[0,\infty]}$ of the state $|n,\ell,m\rangle$ satisfies $P_{n,\ell,m} < 1$, because the perturbation might also induce a transition into another bound state,

$$P_{n,\ell,m} = 1 - \sum_{\ell'=0}^{\infty} \sum_{m'=-\ell'}^{\ell'} \sum_{n'=\ell'+1}^{\infty} |\langle n',\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2.$$

The first order results for $P_{n,\ell,m\to[k_1,k_2],\ell',m'}$, $P_{n,\ell,m\to[k_1,k_2]}$ and $P_{n,\ell,m}$ follow from the first order scattering matrix element

$$\begin{aligned} S^{(1)}_{k,\ell',m';n,\ell,m} &= \langle k,\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle^{(1)} \\ &= -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{\infty} dt\, \exp\left(\frac{\mathrm{i}}{\hbar}\,(E_k - E_n)\,t\right) \langle k,\ell',m'|V(t)|n,\ell,m\rangle \\ &= -\mathrm{i}\frac{\sqrt{2\pi}}{\hbar} \langle k,\ell',m'|V(\omega_{k,n})|n,\ell,m\rangle \end{aligned}$$

with the transition frequency $\omega_{k,n} = (E_k - E_n)/\hbar$. This assumes that the Fourier transformed operator $V(\omega_{k,n})$ exists in the sense of standard Fourier theory. The case of a monochromatic perturbation, for which the Fourier transform is a δ function in frequency space, is discussed in the following subsection.

[4] If the perturbation $V(t)$ contains directional information (e.g. polarization of an incoming photon or the direction of an electric field), then we might also like to calculate probabilities for the direction of dissociation of the hydrogen atom. This direction would be given by the $\boldsymbol{k}$ vector of relative motion between the electron and the proton after separation. For the calculation of directional information we would have to combine the spherical Coulomb waves $|k,\ell,m\rangle$ into states which approximate plane wave states $|\boldsymbol{k}\rangle$ at infinity, similar to the construction of incoming approximate plane wave states in Section 13.5, see also the discussion of the photoeffect in [2].

The Golden Rule for transitions from discrete states into a continuum of states

Assume again that the initial state $|n,\ell,m\rangle$ is a bound state of a rotationally symmetric Hamiltonian H_0 with energy $E_n < 0$. The final state is an unbound state $|E,\ell',m'\rangle$ of H_0 of energy $E > 0$,

$$H_0|E,\ell',m'\rangle = E|E,\ell',m'\rangle.$$

The completeness relation for the eigenstates of H_0 will generically have the form

$$\sum_{n,\ell,m} |n,\ell,m\rangle\langle n,\ell,m| + \sum_{\ell,m} \int_0^\infty dE\, |E,\ell,m\rangle \varrho_\ell(E) \langle E,\ell,m| = 1, \tag{13.25}$$

e.g. for hydrogen we could use $|E,\ell,m\rangle = |k,\ell,m\rangle$ and $\varrho(E) = \Theta(E)k^2 dk/dE$. Equation (13.25) implies that the properly normalized differential probabilities for transitions into the continuous spectrum will have the form

$$\begin{aligned} dP_{n,\ell,m\to E,\ell',m'} &= dE\, \varrho_{\ell'}(E)\, |\langle E,\ell',m'|U_D(\infty,-\infty)|n,\ell,m\rangle|^2 \\ &= dE\, \varrho_{\ell'}(E)\, |S_{E,\ell',m';n,\ell,m}|^2 . \end{aligned}$$

The first order scattering matrix element for a well behaved perturbation $V(t)$ with ordinary Fourier transform $V(\omega)$ is

$$S_{E,\ell',m';n,\ell,m} = -\frac{\mathrm{i}}{\hbar}\sqrt{2\pi}\langle E,\ell',m'|V\left(\frac{E-E_n}{\hbar}\right)|n,\ell,m\rangle$$

and yields well behaved expressions for $dP_{n,\ell,m\to E,\ell',m'}$.
However, the first order scattering matrix element for the monochromatic perturbation[5]

$$V(t) = W\exp(-\mathrm{i}\omega t), \quad V(\omega') = \sqrt{2\pi}W\delta(\omega'-\omega) \tag{13.26}$$

is

$$S_{E,\ell',m';n,\ell,m} = -\frac{\mathrm{i}}{\hbar}2\pi\langle E,\ell',m'|W|n,\ell,m\rangle\delta\left(\frac{E-E_n}{\hbar}-\omega\right). \tag{13.27}$$

This implies a factor

$$\delta(0) = \lim_{\omega\to 0}\delta(\omega) = \lim_{\omega\to 0}\lim_{T\to\infty}\frac{1}{2\pi}\int_{-T/2}^{T/2} dt\, \exp(\mathrm{i}\omega t) = \lim_{T\to\infty}\frac{T}{2\pi}$$

[5]Recall that the notation tacitly implies dependence of the operators V and W on $\mathbf{x}$ and $\mathbf{p}$ (just like we usually write H instead of $H(\mathbf{x},\mathbf{p})$ for a Hamilton operator).

in $dP_{n,\ell,m\to E,\ell',m'}/dE = \varrho_{\ell'}(E)|S_{E,\ell',m';n,\ell,m}|^2$. Dividing by the factor T provides us with a differential transition rate into a final state energy interval $[E, E + dE]$,

$$\begin{aligned} dw_{n,\ell,m\to E,\ell',m'} &= \frac{1}{T} dP_{n,\ell,m\to E,\ell',m'} = dE\, \varrho_{\ell'}(E) \frac{1}{T} |S_{E,\ell',m';n,\ell,m}|^2 \\ &= dE\, \varrho_{\ell'}(E) \frac{2\pi}{\hbar^2} |\langle E,\ell',m'|W|n,\ell,m\rangle|^2\, \delta\left(\frac{E-E_n}{\hbar} - \omega\right) \\ &= dE\, \varrho_{\ell'}(E) \frac{2\pi}{\hbar} |\langle E,\ell',m'|W|n,\ell,m\rangle|^2\, \delta(E - E_n - \hbar\omega). \end{aligned}$$

Integration over the final state energy E then yields an expression for the transition rate,

$$w_{n,\ell,m\to E,\ell',m'} = \frac{2\pi}{\hbar} |\langle E,\ell',m'|W|n,\ell,m\rangle|^2\, \varrho_{\ell'}(E)\Big|_{E=E_n+\hbar\omega},$$

which is commonly referred to as the *Golden Rule*.
The total first order ionization rate of the state $|n,\ell,m\rangle$ under the perturbation (13.26) is then

$$w_{n,\ell,m} = \frac{2\pi}{\hbar} \sum_{\ell'=0}^{\infty} \sum_{m'=-\ell'}^{\ell'} |\langle E,\ell',m'|W|n,\ell,m\rangle|^2\, \varrho_{\ell'}(E)\Big|_{E=E_n+\hbar\omega}.$$

For the hydrogen atom, we have $E = \hbar^2k^2/2\mu$, $|E,\ell,m\rangle = |k,\ell,m\rangle$ are the spherical Coulomb waves, and

$$\varrho(E) = \Theta(E) k^2 \frac{dk}{dE} = \frac{\Theta(E)}{\hbar^3}\sqrt{2\mu^3 E}. \tag{13.28}$$

This differs from (12.12) for $d = 3$ by a missing factor $g/2\pi^2 = g4\pi/8\pi^3$. The spin factor is $g = 1$, because spin flips can usually be neglected in ionization transitions. Inclusion of spin quantum numbers m_s and m_s' for the initial and final states would therefore result in a factor $\delta_{m_s,m_s'}$. There is no factor 4π because the angular directions in $\boldsymbol{k}$ space have been discretized in terms of angular momentum quantum numbers (ℓ', m'), and there is no factor $(2\pi)^{-3}$ because the density in the Golden Rule and in equation (13.28) is a number of states per unit of energy, but it is *not* a number of states per energy and *volume* (remember $V \to (2\pi)^3$ in the contiuum limit). It comes in units $\mathrm{cm}^{-3}\mathrm{eV}^{-1}$ because the projector $|k,\ell,m\rangle\langle k,\ell,m|$ for spherical Coulomb waves has dimension length^3 whence $|\langle k,\ell',m'|W|n,\ell,m\rangle|^2$ comes in units of $\mathrm{cm}^3\mathrm{eV}^2$. Please also recall the remark after equation (12.7).
The standard expression for the Golden Rule for the transition rate from a discrete state $|m\rangle$ into a continuous state $|n\rangle$ due to the perturbation $V = W\exp(-\mathrm{i}\omega t)$ is

$$w_{m\to n} = \int_{-\infty}^{\infty} dE\, \frac{dw_{m\to n}}{dE} = \frac{2\pi}{\hbar} \varrho(E_n) |\langle n|W|m\rangle|^2\Big|_{E_n=E_m+\hbar\omega}. \tag{13.29}$$

This is also particularly popular for time-indendent V,

$$w_{m\to n} = \frac{2\pi}{\hbar}\varrho(E_n)|\langle n|V|m\rangle|^2\Big|_{E_n=E_m} . \tag{13.30}$$

Quantum systems can have degeneracy between states $|m\rangle$ which are labelled by discrete quantum numbers and states $|n\rangle$ with continuous quantum numbers. Metastable states, or excited bound states in many-electron atoms provide examples for this, and equation (13.30) would be the first order expression for the decay rate of these states. An example for this is the Auger effect, which is electron emission from atoms due to Coulomb repulsion. The perturbation operator[6] $V = e^2/4\pi|\mathbf{x}_1 - \mathbf{x}_2|$ is time-independent, and energy conservation is fulfilled because the discrete bound state of two electrons in an excited atom can exceed the sum of ground state energy and ionization energy, see Figure 13.3.

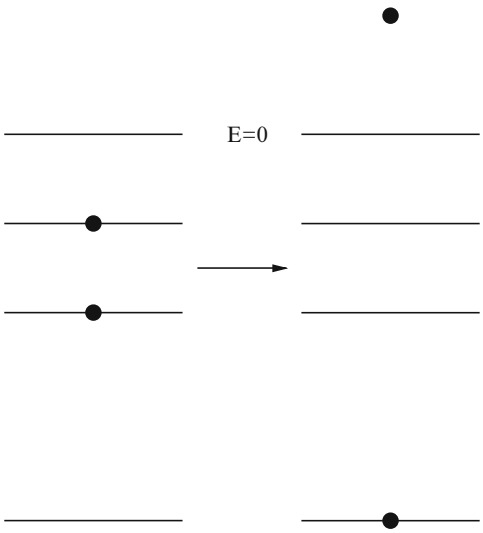


Figure 13.3: Energy schematics for an Auger process. The initial bound state of the two electrons has the same energy as the final continuous state of an ion and a free electron.

Time-dependent perturbation theory in second order and the Golden Rule #1

We will discuss a time-independent perturbation V,

$$H = H_0 + V,$$

[6] G. Wentzel, Z. Phys. 43, 524 (1927).

and transition from a discrete state $|m\rangle$ into a continuous state $|n\rangle$. The completeness relation for the eigenstates of H_0 is

$$\sum_m |m\rangle\langle m| + \int dE_n \varrho(E_n)|n\rangle\langle n| = 1.$$

We will also write this symbolically as

$$\sum\!\!\!\!\!\!\int_l |l\rangle\langle l| = 1.$$

If $\langle n|V|m\rangle = 0$, the leading order term for the scattering matrix element $\langle n|U_D(\infty,-\infty)|m\rangle$ is the second order term

$$S^{(2)}_{nm} = -\frac{1}{\hbar^2}\sum\!\!\!\!\!\!\int_l \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\tau} d\tau' \, \exp(\mathrm{i}\omega_{nl}\tau)\langle n|V|l\rangle \exp(\mathrm{i}\omega_{lm}\tau')\langle l|V|m\rangle.$$

To make the τ' integral convergent, we add a small negative imaginary part to $\omega_{lm} \to \omega_{lm} - \mathrm{i}\epsilon$, so that the time integrals yield

$$\begin{aligned}\int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\tau} d\tau' \, \exp(\mathrm{i}\omega_{nl}\tau)\exp(\mathrm{i}\omega_{lm}\tau' + \epsilon\tau') &= \frac{1}{\mathrm{i}\omega_{lm}+\epsilon}\int_{-\infty}^{\infty} d\tau \, \exp(\mathrm{i}\omega_{nm}\tau) \\ &= \frac{2\pi}{\mathrm{i}\omega_{lm}+\epsilon}\delta(\omega_{nm}). \qquad (13.31)\end{aligned}$$

This yields the second order scattering matrix element

$$S^{(2)}_{nm} = \frac{2\pi\mathrm{i}}{\hbar^2}\delta(\omega_{nm})\sum\!\!\!\!\!\!\int_l \frac{\langle n|V|l\rangle\langle l|V|m\rangle}{\omega_{lm} - \mathrm{i}\epsilon} = 2\pi\mathrm{i}\delta(E_n - E_m)\sum\!\!\!\!\!\!\int_l \frac{\langle n|V|l\rangle\langle l|V|m\rangle}{E_l - E_m - \mathrm{i}\epsilon},$$

and the differential transition rate

$$\begin{aligned} dw_{m\to n} &= dE_n \varrho(E_n)\frac{1}{T}\,|S_{nm}|^2 \\ &= dE_n \varrho(E_n)\frac{2\pi}{\hbar}\delta(E_n - E_m)\left|\sum\!\!\!\!\!\!\int_l \frac{\langle n|V|l\rangle\langle l|V|m\rangle}{E_l - E_m - \mathrm{i}\epsilon}\right|^2. \qquad (13.32)\end{aligned}$$

Integration yields the 2nd order expression for the transition rate,

$$w_{m\to n} = \frac{2\pi}{\hbar}\varrho(E_n)\left|\sum\!\!\!\!\!\!\int_l \frac{\langle n|V|l\rangle\langle l|V|m\rangle}{E_l - E_m - \mathrm{i}\epsilon}\right|^2\Bigg|_{E_n=E_m}. \qquad (13.33)$$

Equation (13.33) tells us how transitions through virtual intermediate states can generate the transition from $|m\rangle$ to $|n\rangle$ even if the direct transition is forbidden due to a selection rule $\langle n|V|m\rangle = 0$.

In his famous lectures on nuclear physics at the University of Chicago in 1949, Fermi coined the phrase "Golden Rule #2" for the first order transition rate (13.29,13.30). He denoted the corresponding second order expression for transition rates as "Golden Rule #1", because it is important for nuclear reactions through intermediate compound nuclei [28].

13.5 Transitions from continuous states into discrete states – recombination or capture cross sections

Transitions from continuous to discrete states arise e.g. in the capture of electrons by ions, in the absorption of an electron from a valence band into an acceptor state in a doped semiconductor, in neutron capture by nuclei etc. Consider e.g. the process $|k,\ell,m\rangle \to |n,\ell',m'\rangle$ of apsorption of an electron by an H^+ ion, where we still assume that the hydrogen Hamiltonian (13.24) for relative motion is perturbed by addition of an operator $V(t)$. From our previous experience, we expect that the transition matrix element

$$S_{n,\ell',m';k,\ell,m} = \langle n,\ell',m'|U_D(\infty,-\infty)|k,\ell,m\rangle$$

yields a measure of probability for the absorption in the form of a transition probability density

$$\mathcal{P}_{k,\ell,m\to n,\ell',m'} = |S_{n,\ell',m';k,\ell,m}|^2 . \tag{13.34}$$

Indeed, the dimensionless number

$$\begin{aligned} P_{n,\ell',m'} &= \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\int_0^\infty dk\, k^2\, |\langle n,\ell',m'|U_D(\infty,-\infty)|k,\ell,m\rangle|^2 \\ &= 1 - \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\sum_{n'=\ell+1}^{\infty} |\langle n,\ell',m'|U_D(\infty,-\infty)|n',\ell,m\rangle|^2 \end{aligned}$$

is the probability that the state $|n,\ell',m'\rangle$ emerged from some capture ($p^+ + e^- \to H$) event rather than from an internal transition in the hydrogen atom. However, a better use of the transition matrix elements from continuous initial states for comparison with experiments is the calculation of cross sections. One possibility to calculate capture or absorption due to a Coulomb potential is to use parabolic coordinates because the incoming asymptotic plane wave can be described in parabolic coordinates, just like in Rutherford scattering [2]. However, radial coordinates are just as convenient for this problem.

Calculation of the capture cross section

We will outline how to calculate the first order cross section for the reaction $p^+ + e^- \to H$ due to a monochromatic perturbation $V(t) = W\exp(\mathrm{i}\omega t)$. For a judicious choice of the operator $W \equiv W(\mathbf{p},\mathbf{x})$ this describes electron-proton recombination due to emission of a photon with energy $\hbar\omega$. We will discuss these operators in Chapter 18, but here we do not specify the operator W further. Our present focus is rather to develop the formalism for calculating the capture or recombination cross section for a general perturbation

$W(\mathbf{p},\mathbf{x})\exp(\mathrm{i}\omega t)$. We should also mention that perturbations $V(t)=V(\mathbf{x},t)$ due to interactions with additional nearby electrons or ions are much more efficient and therefore more important for electron capture than direct radiative recombination due to photon emission.
The wave function for the approach between a free electron and a proton in the effective single particle description for relative motion is given by the wave function $\langle \boldsymbol{x}|k\rangle_{MG}$ which was constructed by Mott and Gordon in 1928 (7.70). The normalization factor is irrelevant because it cancels in the cross section. For convenience, it was chosen in equation (7.70) such that the asymptotic incoming current density is

$$j_{in}=\frac{\hbar k}{\mu}, \tag{13.35}$$

where μ is the reduced mass of the two-particle system. This current density has units of $\mathrm{cm/s}=\mathrm{cm}^{-2}\mathrm{s}^{-1}/\mathrm{cm}^{-3}$ because it is a current density per unit of volume in $\boldsymbol{k}$ space, which is a consequence of the use of an asymptotic plane wave state in its calculation. A current density per $\boldsymbol{k}$ space volume is the correct notion for the calculation of the electron-proton recombination cross section, because the S matrix element

$$S_{n,\ell,m;k}=\frac{2\pi}{\mathrm{i}\hbar}\langle n,\ell,m|W|k\rangle_{MG}\delta(\omega_{nk}+\omega)$$

yields a transition probability density per $\boldsymbol{k}$ space volume

$$\mathcal{P}_{k\to n,\ell,m}=\left|S_{n,\ell,m;k}\right|^2$$

which comes in units of cm^3, again due to the use of an asymptotic plane wave state as incoming state.
$\mathcal{P}_{k\to n,\ell,m}$ contains the factor

$$\delta(0)=\lim_{\omega\to 0}\delta(\omega)=\lim_{\omega\to 0}\lim_{T\to\infty}\frac{1}{2\pi}\int_{-T/2}^{T/2}dt\,\exp(\mathrm{i}\omega t)=\lim_{T\to\infty}\frac{T}{2\pi}.$$

We can use this to calculate a transition rate density per $\boldsymbol{k}$ space volume

$$\mathcal{W}_{k\to n,\ell,m}=\frac{1}{T}\left|S_{n,\ell,m;k}\right|^2=\frac{2\pi}{\hbar^2}\left|\langle n,\ell,m|W|k\rangle_{MG}\right|^2\delta(\omega_{nk}+\omega)\,. \tag{13.36}$$

The transition rate is certainly proportional to the asymptotic current density j_{in}, and therefore we divide the transition rate density by this current density to get a measure for the probability of the absorption process $|k\rangle_{MG}\to|n,\ell,m\rangle$. This yields the absorption cross section

$$\sigma_{k\to n,\ell,m}=\frac{\mathcal{W}_{k\to n,\ell,m}}{j_{in}}=\frac{2\pi\mu}{\hbar^3 k}\left|\langle n,\ell,m|W|k\rangle_{MG}\right|^2\delta(\omega_{nk}+\omega) \tag{13.37}$$

with units of cm^2. The total absorption cross section due to the perturbation operator $W(\mathbf{p}, \mathbf{x}) \exp(\mathrm{i}\omega t)$ is then

$$\sigma_k = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \sum_{n=\ell+1}^{\infty} \sigma_{k\to n,\ell,m}.$$

The capture cross section enters into the calculations of rate coefficients $(\sigma v)_{av}$, where the notation indicates averaging over the distribution of relative particle velocities in a plasma of ions and electrons. The rate coefficients go into the balance equations for electron and ion densities,

$$\frac{d\rho_e}{dt} = \frac{d\rho_p}{dt} = -(\sigma v)_{av} \rho_p \rho_e,$$

where in general additional terms due to collisional relaxation and ionization have to be included. Due to (13.35) the rate coefficients are directly related to the transition rates per $\boldsymbol{k}$ space volume calculated in the state (7.70),

$$v\sigma_k = j_{in}\sigma_k = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \sum_{n=\ell+1}^{\infty} \mathcal{W}_{k\to n,\ell,m}.$$

Calculations of radiative capture cross sections for electron-proton recombination into arbitrary hydrogen shells were performed in parabolic coordinates by Oppenheimer[7] and by Bethe and Salpeter [2]. Calculations in polar coordinates had been performed by Wessel, Stückelberg and Morse, and Stobbe[8]. All these authors had noticed that the electron capture cross sections for ions from radiative recombination were much too small to explain the experimental values, and it was eventually recognized that collisional relaxation due to interactions with spectator particles dominated the observed recombination rates. Therefore modern calculations of electron-ion recombination rates focus on collisional relaxation, which means that the relevant perturbation operators V are not determined by photon emission but by Coulomb interactions in a plasma, and the spectator particles also have to be taken into account in the initial and final states. Electron-ion recombination rates are particularly important for plasma physics and astrophysics.

13.6 Transitions between continuous states – scattering cross sections

For transitions between continuous states, e.g. $|\boldsymbol{k}\rangle \to |\boldsymbol{k}'\rangle$, the S matrix element

$$S_{\boldsymbol{k}',\boldsymbol{k}} = \langle \boldsymbol{k}' | U_D(\infty, -\infty) | \boldsymbol{k} \rangle$$

[7] J.R. Oppenheimer, Z. Phys. 55, 725 (1929).

[8] W. Wessel, Annalen Phys. 397, 611 (1930); E.C.G. Stückelberg & P.M. Morse, Phys. Rev. 36, 16 (1930); M. Stobbe, Annalen Phys. 399, 661 (1930).

is a quantity with the dimension length^3, because both external states have dimension length$^{3/2}$. However, we know from Section 13.4 how to make sense of transition matrix elements with continuous final states, viz. as transition probability densities $d^3\boldsymbol{k}'|S_{\boldsymbol{k}',\boldsymbol{k}}|^2$ in the final state space. We also know from Section 13.5 that continuous initial states call for normalization of $|S_{\boldsymbol{k}',\boldsymbol{k}}|^2$ by the reaction time T and the current density j_{in} of incident particles to calculate a cross section for the quantum mechanical reaction described by the S matrix element, see equations (13.36,13.37). Our previous experience with initial or final continuous states therefore motivates the definition of the *differential scattering cross section*

$$d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} = d^3\boldsymbol{k}' \frac{|S_{\boldsymbol{k}',\boldsymbol{k}}|^2}{T j_{in}}. \tag{13.38}$$

This has again the dimension length^2, because the incident current density j_{in} for plane waves has units of cm/s, see equation (13.35) and the following discussion.
The notion of a differential scattering cross section is sufficiently important to warrant rederivation of equation (13.38) in simple steps in the next paragraph.

Cross section for scattering off a periodic perturbation

We apply the transition probability between continuous states to calculate the scattering cross section for a monochromatic perturbation $V(t) = W\exp(-\mathrm{i}\omega t)$. Our Hamiltonian is

$$H = \frac{\mathbf{p}^2}{2m} + W(\mathbf{x})\exp(-\mathrm{i}\omega t),$$

and our unperturbed states are plane waves $|\boldsymbol{k}\rangle$.
The first order result for the scattering matrix $S_{\boldsymbol{k}',\boldsymbol{k}} = \langle\boldsymbol{k}'|U_D(\infty,-\infty)|\boldsymbol{k}\rangle$ is

$$\begin{aligned} S_{\boldsymbol{k}',\boldsymbol{k}} &= -\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty} dt\, \exp\left[\mathrm{i}\left(\hbar\frac{k'^2-k^2}{2m} - \omega\right)t\right]\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle \\ &= -\frac{2\pi\mathrm{i}}{\hbar}\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\delta\left(\hbar\frac{k'^2-k^2}{2m} - \omega\right) \\ &= -\mathrm{i}\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}\delta\left(\hbar\frac{k'^2-k^2}{2m} - \omega\right). \end{aligned} \tag{13.39}$$

The transition probability density

$$\mathcal{P}_{\boldsymbol{k}\to\boldsymbol{k}'} = |S_{\boldsymbol{k}',\boldsymbol{k}}|^2 = |\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}|^2\,\delta(0)\delta\left(\hbar\frac{k'^2-k^2}{2m} - \omega\right)$$

contains the factor

$$\delta(0) = \lim_{\omega\to 0}\delta(\omega) = \lim_{\omega\to 0}\lim_{T\to\infty}\frac{1}{2\pi}\int_{-T/2}^{T/2} dt\,\exp(\mathrm{i}\omega t) = \lim_{T\to\infty}\frac{T}{2\pi},$$

and we can calculate a transition rate density

$$\begin{aligned}\mathcal{W}_{\boldsymbol{k}\to\boldsymbol{k}'} &= \frac{1}{T}\left|S_{\boldsymbol{k}',\boldsymbol{k}}\right|^2 = \frac{\left|\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}\right|^2}{2\pi}\delta\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right)\\ &= \frac{2\pi}{\hbar^2}\left|\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\right|^2\delta\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right).\end{aligned}$$

The corresponding differential transition rate into the final state volume $d^3\boldsymbol{k}'$ is

$$dw_{\boldsymbol{k}\to\boldsymbol{k}'} = d^3\boldsymbol{k}'\,\mathcal{W}_{\boldsymbol{k}\to\boldsymbol{k}'} = d^3\boldsymbol{k}'\,\frac{1}{T}\left|S_{\boldsymbol{k}',\boldsymbol{k}}\right|^2.$$

However, this still comes in units of cm^3/s instead of s^{-1}, due to the initial plane wave state. For initial continuous states, we do not apply a volume measure (here $d^3\boldsymbol{k}$) in the space of initial states, but normalize by the current density of the incident particles. This yields a differential cross section for scattering of momentum eigenstates,

$$d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} = \frac{dw_{\boldsymbol{k}\to\boldsymbol{k}'}}{j_{in}} = d^3\boldsymbol{k}'\,\frac{2\pi}{\hbar^2 j_{in}}\left|\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\right|^2\delta\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right). \tag{13.40}$$

The motivation for dividing out the current density j_{in} of incoming particles from the scattering rate is the trivial dependence of the scattering rate on this parameter: if we double the number of incoming particles per second or per cm^2, we will trivially double the number of scattering events per second. Therefore all the interesting physics is in the proportionality factor $d\sigma$ between j_{in} and dw. This proportionality factor has the dimension of an area, and in classical mechanics, integration of $d\sigma$ over $d^3\boldsymbol{p}'$ for scattering of classical particles off a hard sphere of radius r yields the cross section area of the sphere $\sigma = \int d\sigma = \pi r^2$. Therefore the name *differential scattering cross section* for $d\sigma$.

The current density $\boldsymbol{j} = (\hbar/2\mathrm{i}m)(\psi^+\boldsymbol{\nabla}\psi - \boldsymbol{\nabla}\psi^+\cdot\psi)$ for a plane wave, $\boldsymbol{j} = \hbar\boldsymbol{k}/(2\pi)^3 m$, is actually a current density per unit of volume in $\boldsymbol{k}$-space. This is the correct current density to be used in (13.40), because $dw_{\boldsymbol{k}\to\boldsymbol{k}'}$ is a transition rate per unit of volume in $\boldsymbol{k}$-space, and the ratio yields a *bona fide* differential cross section[9]. Expressed in terms of continuum plane wave matrix elements, the differential scattering cross section is

$$\begin{aligned}d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} &= d^3\boldsymbol{k}'\,\frac{(2\pi)^4 m}{\hbar^3 k}\left|\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\right|^2\delta\left(\hbar\frac{k'^2-k^2}{2m}-\omega\right)\\ &= d^3\boldsymbol{k}'\,(2\pi)^4\frac{2m^2}{\hbar^4 k}\left|\langle\boldsymbol{k}'|W|\boldsymbol{k}\rangle\right|^2\delta\left(k'^2-k^2-\frac{2m}{\hbar}\omega\right).\end{aligned} \tag{13.41}$$

[9] Alternatively, we could have used box normalization for the incoming plane waves, $\langle\boldsymbol{x}|\boldsymbol{k}\rangle = \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})/\sqrt{V}$ both in $dw_{\boldsymbol{k}\to\boldsymbol{k}'}$ and in $\boldsymbol{j}$ ($\Rightarrow \boldsymbol{j} = \hbar\boldsymbol{k}/(mV) = \boldsymbol{v}/V$), or we could have rescaled both $dw_{\boldsymbol{k}\to\boldsymbol{k}'}$ and $\boldsymbol{j}$ with the conversion factor $8\pi^3/V$ to make both quantities separately dimensionally correct, $[dw_{\boldsymbol{k}\to\boldsymbol{k}'}] = \mathrm{s}^{-1}$, $[\boldsymbol{j}] = \mathrm{cm}^{-2}\mathrm{s}^{-1}$. All three methods yield the same dimensionally correct result for the scattering cross section, of course.

We can use the δ-function in (13.41) to integrate over k'. This leaves us with a differential cross section per unit of solid angle,

$$\frac{d\sigma}{d\Omega} = (2\pi)^4 \frac{m^2}{\hbar^4} \sqrt{1 + \frac{2m\omega}{\hbar k^2}} \, |\langle \boldsymbol{k}'|W|\boldsymbol{k}\rangle|^2 \Big|_{k'=\sqrt{k^2+\frac{2m\omega}{\hbar}}} . \tag{13.42}$$

The corresponding result for $\omega = 0$ (scattering off a static potential) can also be derived within the framework of the time-independent Schrödinger equation, see Chapter 11. For the comparison note that

$$\langle \boldsymbol{k}'|W(\mathbf{x})|\boldsymbol{k}\rangle = \frac{1}{(2\pi)^3} \int d^3\boldsymbol{x} \, \exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}] W(\boldsymbol{x}) = \frac{1}{\sqrt{2\pi}^3} W(\Delta\boldsymbol{k})$$

is the Fourier transform of $W(\boldsymbol{x})$ at the momentum transfer $\Delta\boldsymbol{k} = \boldsymbol{k}' - \boldsymbol{k}$. Therefore we can write the differential scattering cross section (13.42) as

$$\frac{d\sigma}{d\Omega} = \sqrt{1 + \frac{2m\omega}{\hbar k^2}} \left| \sqrt{2\pi} \frac{m}{\hbar^2} W(\Delta\boldsymbol{k}) \right|^2 = \sqrt{1 + \frac{2m\omega}{\hbar k^2}} \, |f(\Delta\boldsymbol{k})|^2 , \tag{13.43}$$

with the scattering amplitude

$$f(\Delta\boldsymbol{k}) = -\sqrt{2\pi} \frac{m}{\hbar^2} W(\Delta\boldsymbol{k}), \tag{13.44}$$

cf. (11.16), i.e. equation (13.43) reduces to (11.20) for scattering off a static potential if $\omega = 0$. The full correspondence between the definitions (13.38) of time-dependent perturbation theory and (11.2) of potential scattering theory for time-independent perturbations V follows from the comparison of equations (11.17,11.18) and (13.39),

$$|\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}|^2 = \frac{4\pi^2}{\hbar^2} |\langle \boldsymbol{k}'|V|\boldsymbol{k}\rangle|^2 = \frac{\hbar^2}{4\pi^2 m^2} |f(\Delta\boldsymbol{k})|^2 = \frac{2\pi\hbar}{mk} \lim_{r\to\infty} r^2 j_{out}.$$

The potential scattering formalism could be extended to time-dependent perturbations by using the asymptotic expansion of the time-dependent retarded Green's function (11.39). However, the equivalent scattering matrix formalism is easier to handle.

Scattering theory in second order

We will discuss scattering off the time-independent potential V in second order. The Hamiltonian is

$$H = \frac{\mathbf{p}^2}{2m} + V.$$

If $\boldsymbol{k}' \neq \boldsymbol{k}$ and $\langle \boldsymbol{k}'|V|\boldsymbol{k}\rangle = 0$, the leading order term for the S-matrix is the second order term

$$S_{\boldsymbol{k}',\boldsymbol{k}} = -\frac{1}{\hbar^2} \int d^3\boldsymbol{q} \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\tau} d\tau' \, \exp\left(\frac{\mathrm{i}\hbar}{2m} \left(k'^2 - q^2\right) \tau \right)$$
$$\times \langle \boldsymbol{k}'|V|\boldsymbol{q}\rangle \exp\left(\frac{\mathrm{i}\hbar}{2m} \left(q^2 - k^2\right) \tau' \right) \langle \boldsymbol{q}|V|\boldsymbol{k}\rangle.$$

To make the τ' integral convergent, we add a term $\epsilon\tau'$ in the exponent, so that the time integrals yield

$$\begin{aligned}
&\int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\tau} d\tau' \, \exp\left(\frac{\mathrm{i}\hbar}{2m}\left(k'^2 - q^2\right)\tau\right) \exp\left(\frac{\mathrm{i}\hbar}{2m}\left(q^2 - k^2\right)\tau' + \epsilon\tau'\right) \\
&= \frac{1}{\frac{\mathrm{i}\hbar}{2m}\left(q^2 - k^2\right) + \epsilon} \int_{-\infty}^{\infty} d\tau \, \exp\left(\frac{\mathrm{i}\hbar}{2m}\left(k'^2 - k^2\right)\tau\right) \\
&= \frac{2\pi}{\frac{\mathrm{i}\hbar}{2m}\left(q^2 - k^2\right) + \epsilon} \delta\left(\frac{\hbar}{2m}\left(k'^2 - k^2\right)\right)
\end{aligned}$$

and

$$\begin{aligned}
S_{\boldsymbol{k}',\boldsymbol{k}} &= \frac{2\pi\mathrm{i}}{\hbar^2}\delta(\omega(k') - \omega(k)) \int d^3\boldsymbol{q} \, \frac{\langle \boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle \boldsymbol{q}|V|\boldsymbol{k}\rangle}{\omega(q) - \omega(k) - \mathrm{i}\epsilon} \\
&= 2\pi\mathrm{i}\delta(E(k') - E(k)) \int d^3\boldsymbol{q} \, \frac{\langle \boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle \boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q) - E(k) - \mathrm{i}\epsilon}.
\end{aligned}$$

The corresponding differential transition rate is

$$\begin{aligned}
dw_{\boldsymbol{k}\to\boldsymbol{k}'} &= d^3\boldsymbol{k}' \frac{1}{T} \left|S_{\boldsymbol{k}',\boldsymbol{k}}\right|^2. \\
&= d^3\boldsymbol{k}' \frac{2\pi}{\hbar}\delta(E(k') - E(k)) \left| \int d^3\boldsymbol{q} \, \frac{\langle \boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle \boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q) - E(k) - \mathrm{i}\epsilon} \right|^2,
\end{aligned}$$

and the differential cross section for scattering of momentum eigenstates in second order is

$$\begin{aligned}
d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} &= \frac{dw_{\boldsymbol{k}\to\boldsymbol{k}'}}{j_{in}} \\
&= d^3\boldsymbol{k}' \frac{(2\pi)^4 m}{\hbar^2 k}\delta(E(k') - E(k)) \left| \int d^3\boldsymbol{q} \, \frac{\langle \boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle \boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q) - E(k) - \mathrm{i}\epsilon} \right|^2 \\
&= d^3\boldsymbol{k}' \frac{(2\pi)^4 m^2}{\hbar^4 k k'}\delta(k' - k) \left| \int d^3\boldsymbol{q} \, \frac{\langle \boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle \boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q) - E(k) - \mathrm{i}\epsilon} \right|^2. \qquad (13.45)
\end{aligned}$$

Integration over k' yields the differential scattering cross section per unit of solid angle in second order,

$$\frac{d\sigma}{d\Omega} = (2\pi)^4 \frac{m^2}{\hbar^4} \left| \int d^3\boldsymbol{q} \, \frac{\langle \boldsymbol{k}'|V|\boldsymbol{q}\rangle\langle \boldsymbol{q}|V|\boldsymbol{k}\rangle}{E(q) - E(k) - \mathrm{i}\epsilon} \right|^2 \Bigg|_{k'=k}. \qquad (13.46)$$

Equations (13.42) and (13.46) could be denoted as Fermi's Golden Rules #2 and #1 for scattering theory.

13.7 Expansion of the scattering matrix to higher orders

For time-independent perturbation V we can write the expansion of the scattering matrix in the form

$$\begin{aligned}
S_{fi}(t,t') &= \langle f|U_D(t,t')|i\rangle = \langle f|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right)|i\rangle \\
&= \sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t}d\tau_1\int_{t'}^{\tau_1}d\tau_2\ldots\int_{t'}^{\tau_{n-1}}d\tau_n\,\langle f|U_0(t_0,\tau_1)VU_0(\tau_1,\tau_2) \\
&\quad\times VU_0(\tau_2,\tau_3)\ldots U_0(\tau_{n-1},\tau_n)VU_0(\tau_n,t_0)|i\rangle \\
&= \sum_{n=0}^{\infty}\sum\!\!\!\!\!\!\int_{j_1,\ldots j_{n-1}}\frac{1}{(\mathrm{i}\hbar)^n}\int_{t'}^{t}d\tau_1\int_{t'}^{\tau_1}d\tau_2\ldots\int_{t'}^{\tau_{n-1}}d\tau_n\,\exp\left(-\frac{\mathrm{i}}{\hbar}E_f t_0\right) \\
&\quad\times\exp\left(\frac{\mathrm{i}}{\hbar}E_f\tau_1\right)V_{fj_1}\exp\left(-\frac{\mathrm{i}}{\hbar}E_{j_1}\tau_1\right)\exp\left(\frac{\mathrm{i}}{\hbar}E_{j_1}\tau_2\right)V_{j_1j_2} \\
&\quad\times\exp\left(-\frac{\mathrm{i}}{\hbar}E_{j_2}\tau_2\right)\exp\left(\frac{\mathrm{i}}{\hbar}E_{j_2}\tau_3\right)\ldots\exp\left(\frac{\mathrm{i}}{\hbar}E_{j_{m-1}}\tau_m\right)V_{j_{m-1}j_m} \\
&\quad\times\exp\left(-\frac{\mathrm{i}}{\hbar}E_{j_m}\tau_m\right)\ldots\exp\left(\frac{\mathrm{i}}{\hbar}E_{j_{n-2}}\tau_{n-1}\right)V_{j_{n-2}j_{n-1}} \\
&\quad\times\exp\left(-\frac{\mathrm{i}}{\hbar}E_{j_{n-1}}\tau_{n-1}\right)\exp\left(\frac{\mathrm{i}}{\hbar}E_{j_{n-1}}\tau_n\right)V_{j_{n-1}i}\exp\left(-\frac{\mathrm{i}}{\hbar}E_i\tau_n\right) \\
&\quad\times\exp\left(\frac{\mathrm{i}}{\hbar}E_i t_0\right).
\end{aligned}$$

Setting $t'\to-\infty$ and $t\to\infty$, we find the equation

$$\begin{aligned}
S_{fi} &= \delta_{fi} - 2\pi\mathrm{i}\delta(E_f-E_i)V_{fi} - 2\pi\mathrm{i}\delta(E_f-E_i) \\
&\quad\times\sum_{n=2}^{\infty}\sum\!\!\!\!\!\!\int_{j_1,\ldots j_{n-1}} V_{fj_1}V_{j_1j_2}\ldots V_{j_{n-2}j_{n-1}}V_{j_{n-1}i}\left[(E_i-E_{j_1}+\mathrm{i}\epsilon)\right. \\
&\quad\times\left.(E_i-E_{j_2}+\mathrm{i}\epsilon)\ldots(E_i-E_{j_{n-2}}+\mathrm{i}\epsilon)(E_i-E_{j_{n-1}}+\mathrm{i}\epsilon)\right]^{-1}. \quad (13.47)
\end{aligned}$$

However, we can also use

$$\begin{aligned}
-2\pi\mathrm{i}\delta(E_f-E_i) &= -\frac{\mathrm{i}}{\hbar}\lim_{\epsilon\to0,t\to\infty,\epsilon t\to0}\int_{-\infty}^{t}d\tau\,\exp\left(\frac{\mathrm{i}(E_f-E_i)+\epsilon}{\hbar}\tau\right) \\
&= \lim_{\epsilon\to0,t\to\infty,\epsilon t\to0}\frac{1}{E_i-E_f+\mathrm{i}\epsilon}\exp\left(\frac{\mathrm{i}(E_f-E_i)t+\epsilon t}{\hbar}\right).
\end{aligned}$$

This yields a form which is very similar to the expressions for the shifts of wave functions in time-independent perturbation theory,

$$S_{fi} = \lim_{\epsilon\to 0, t\to\infty, \epsilon t\to 0} \exp\left(\frac{\mathrm{i}(E_f - E_i)t + \epsilon t}{\hbar}\right)\left(\delta_{fi} + \frac{V_{fi}}{E_i - E_f + \mathrm{i}\epsilon}\right.$$
$$\left. + \sum_{n=2}^{\infty} \sum\!\!\!\!\!\!\int_{j_1,\ldots j_{n-1}} V_{fj_1} V_{j_1 j_2} \ldots V_{j_{n-2} j_{n-1}} V_{j_{n-1} i} \left[(E_i - E_f + \mathrm{i}\epsilon)\right.\right.$$
$$\left.\left. \times (E_i - E_{j_1} + \mathrm{i}\epsilon) \ldots (E_i - E_{j_{n-2}} + \mathrm{i}\epsilon)(E_i - E_{j_{n-1}} + \mathrm{i}\epsilon)\right]^{-1}\right).$$

If the initial state is continuous, $|S_{fi}|^2$ will enter into the calculation of cross sections. If only the final state is continuous, $|S_{fi}|^2$ will enter into the calculation of decay rates. If both external states are discrete, the perturbation V should be treated as arising from a quantum field, see the remarks at the end of Section 13.3.

13.8 Problems

13.1 Use Fourier transformation to calculate the matrix elements $\langle x|U(t)|x'\rangle$ for the free time evolution operator in one dimension. Compare with the result (13.7) for the harmonic oscillator.

13.2 Calculate the annihilation and creation operators $a(t)$ and $a^+(t)$ of the harmonic oscillator in the Heisenberg picture.
Use the previous results to calculate the operators $\mathrm{x}(t)$ and $\mathrm{p}(t)$ for the harmonic oscillator in the Heisenberg picture.

13.3 Calculate the first order transition probability for the transition 1s→2p for a hydrogen atom which is perturbed by a potential

$$V(t) = P\frac{\mathrm{z}}{2\tau}\exp(-|t|/\tau).$$

P and τ are constants. What is the meaning of P in the limit $\tau \to 0$?

13.4 The Golden Rule #2 for the first order transition rate (13.29) is often abused for the discussion of transitions between discrete states. In this problem you will be asked to figure out where the drivation of the Golden Rule #2 for transitions between discrete states breaks down.
13.4a Calculate the first order transition probability for transitions between discrete energy eigenstates $|m\rangle \to |n\rangle$ under the influence of a monochromatic perturbation $V(t) = W\exp(-\mathrm{i}\omega t)$ which only acts between times t' and t. Which consistency requirements do you find from the condition that the first order result describes a transition probability $P_{m\to n}(t, t')$? Calculate also the transition rate $w_{m\to n}(t, t') = dP_{m\to n}(t, t')/dt$.
13.4b Try to take the limit $t - t' \to \infty$ to derive the Golden Rule #2. Does

this comply with the consistency requirements from 13.4a?
13.4c Why do the inconsistencies of 13.4b not appear if the final state $|n\rangle$ is a continuous state?

Solution to Problem 4

For a periodic perturbation $V(t) = W\exp(-\mathrm{i}\omega t)$ the first order transition amplitude between times t' and t, and between different eigenstates of H_0 becomes

$$\begin{aligned}\langle n|U_D(t,t')|m\rangle &\approx -\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, \exp[\mathrm{i}(\omega_{nm}-\omega)\tau]\langle n|W|m\rangle \\ &= \frac{\exp[\mathrm{i}(\omega_{nm}-\omega)t'] - \exp[\mathrm{i}(\omega_{nm}-\omega)t]}{\hbar(\omega_{nm}-\omega)}\langle n|W|m\rangle.\end{aligned}$$

The resulting transition probability is

$$\begin{aligned}P_{m\to n}(t-t') &= 2\frac{1-\cos[(\omega_{nm}-\omega)(t-t')]}{\hbar^2(\omega_{nm}-\omega)^2}|\langle n|W|m\rangle|^2 \\ &= \left(\frac{2\sin[(\omega_{nm}-\omega)(t-t')/2]}{\hbar(\omega_{nm}-\omega)}|\langle n|W|m\rangle|\right)^2, \end{aligned} \tag{13.48}$$

and the rate of change of the transition probability follows as

$$w_{m\to n}(\Delta t) = \frac{d}{dt}P_{m\to n}(\Delta t) = \frac{2}{\hbar^2}\frac{\sin[(\omega_{nm}-\omega)\Delta t]}{\omega_{nm}-\omega}|\langle n|W|m\rangle|^2. \tag{13.49}$$

Equations (13.48) and (13.49) yield perfectly well behaved, dimensionally correct expressions for the first order transition probability and transition rate between discrete states. Consistency with the probability interpretation for the extreme case $\omega_{nm}-\omega = 0$ requires

$$\Delta t = t - t' \le \frac{\hbar}{|\langle n|W|m\rangle|}, \tag{13.50}$$

or alternatively, consistency of (13.48) with the probability interpretation for arbitrary Δt requires

$$|\omega_{nm}-\omega| \ge \frac{2}{\hbar}|\langle n|W|m\rangle|. \tag{13.51}$$

The problem arises with the limit $\Delta t\to\infty$, which would transform the transition rate from an ordinary function of frequencies into a δ function,

$$\begin{aligned}w_{m\to n} &= \lim_{\Delta t\to\infty} w_{m\to n}(\Delta t) = \frac{2\pi}{\hbar^2}|\langle n|W|m\rangle|^2\delta(\omega_{nm}-\omega) \\ &= \frac{2\pi}{\hbar}|\langle n|W|m\rangle|^2\delta(E_n-E_m-\hbar\omega). \end{aligned} \tag{13.52}$$

Here we used

$$\begin{aligned}\lim_{\Delta t\to\infty}\frac{\sin[(\omega_{nm}-\omega)\Delta t]}{\omega_{nm}} &= \lim_{\Delta t\to\infty}\frac{1}{2}\int_{-\Delta t}^{\Delta t} d\tau\, \exp[\mathrm{i}(\omega_{nm}-\omega)\tau] \\ &= \pi\delta(\omega_{nm}-\omega) = \pi\hbar\delta(E_n-E_m-\hbar\omega).\end{aligned}$$

Taking the limit $\Delta t \to \infty$ violates either the condition (13.50), or the condition (13.51) through its result $\omega_{nm} - \omega \to 0$ for a transition. From this point of view (and ignoring the fact that we should have at least one continuous external state when properly taking into account photons, Section 18.5), the resolution of the paradox of emergence of a δ function between discrete states in the limit $\Delta t \to \infty$ is that in the region of frequencies (13.51) where the first order result might be applicable, the first order result becomes subdominant for large Δt and (at the very least) higher order terms would have to be included to get estimates of transition probabilities and transition rates, or perturbation theory is just not suitable any more to get reliable estimates for those parameters.
These problems do not arise for continuous final states, because in these cases $P_{m\to n}(t,t') \to dP_{m\to n}(t,t') = dE_n \varrho(E_n)|S_{n,m}(t,t')|^2$ are not transition probabilities any more (which would be bounded by 1), but only transition probability densities for which only the integral over the energy scale with measure factor $\varrho(E_n)$ is bounded.

13.5 Calculate the cross section for recombination of an electron and a proton with energy $\hbar^2 k^2/2\mu$ (in their relative motion) into the ground state of hydrogen. Perform the calculation both in parabolic and in polar coordinates.

Chapter 14

Path Integrals in Quantum Mechanics

Path integrals provide in many instances an elegant complementary description of quantum mechanics and also for the quantization of fields, which we will study from a canonical point of view in Chapter 17 and following chapters. Path integrals are particularly popular in scattering theory, because the techniques of path integration were originally developed in the study of time evolution operators. Other areas where path integrals are used include statistical physics and the description of dissipative systems.

Path integration is based on a beautiful intuitive description of the quantum mechanical time evolution of particles or wave functions from initial to final states. The prize for the intuitive elegance in the description of time evolution is that the description of bound systems and the identification of the corresponding states is often cumbersome with path integral methods. On the other hand, path integration and canonical quantization complement each other particularly well in relativistic scattering theory, where canonical methods are needed for unitarity of the scattering matrix, for the normalization of the scattering states, and also for the correct choice of propagators in perturbation theory, while the path integral formulation provides an elegant tool for the development of rules for covariant perturbation theory.

Path integrals had been developed by Richard Feynman as a tool for understanding the role of the classical action in quantum mechanics, and had then evolved into a basis for covariant perturbation theory in relativistic field theories[1]. Our introductory exposition will focus on the use of path integrals in scattering theory. The first authoritative textbook on path integrals was coauthored by Feynman himself [9]. Extensive discussions and many applications of path integrals can be found in [12] and [21]. The use of path integrals in perturbative relativistic quantum field theory from a particle physics perspective is discussed e.g. in [16, 29, 39].

[1] R.P. Feynman, Ph.D. thesis, Princeton University 1942; Rev. Mod. Phys. 20, 367 (1948).

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14.1 Time evolution in the path integral formulation

The standard formulation of path integrals derives from the time evolution of states in the $\boldsymbol{x}$ representation,

$$\langle \boldsymbol{x}|\psi(t)\rangle = \langle \boldsymbol{x}|U(t,t_0)|\psi(t_0)\rangle,$$

We can also write this as

$$\langle \boldsymbol{x}|\psi(t)\rangle = \langle \boldsymbol{x},t,t_0|\psi(t_0)\rangle$$

if we define the time-dependent states

$$|\boldsymbol{x},t,t_0\rangle = U^+(t,t_0)|\boldsymbol{x}\rangle = \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_t^{t_0} d\tau\, H(\tau)\right)|\boldsymbol{x}\rangle. \tag{14.1}$$

The parameter t_0 is usually suppressed in the notation of states, $|\boldsymbol{x},t,t_0\rangle \equiv |\boldsymbol{x},t\rangle$, $|\psi(t_0)\rangle \equiv |\psi\rangle$. Note that the time-dependent basis states (14.1) are just the eigenstates of the Heisenberg picture operator

$$\mathbf{x}(t) = U^+(t,t_0)\mathbf{x}U(t,t_0),$$

and the time parameter t_0 is the time parameter where the Schrödinger picture and the Heisenberg picture coincide. The Heisenberg picture eigenstates satisfy the completeness relation

$$\int d^3\boldsymbol{x}\,|\boldsymbol{x},t\rangle\langle\boldsymbol{x},t| = 1 \tag{14.2}$$

as a consequence of the completeness relation of the $\mathbf{x}$ eigenstates $|\boldsymbol{x}\rangle$ and the unitarity of the time evolution operators. Furthermore, the composition property (13.5) of time evolution operators implies that the products of the Heisenberg picture eigenstates yield the $\boldsymbol{x}$ representation of the time evolution operator,

$$\langle \boldsymbol{x},t|\boldsymbol{x}',t'\rangle = \langle \boldsymbol{x}|U(t,t')|\boldsymbol{x}'\rangle. \tag{14.3}$$

The properties (14.2) and (14.3) imply the following representation of the time evolution of a state,

$$\begin{aligned}\langle \boldsymbol{x},t|\psi\rangle &= \langle \boldsymbol{x},t|\left(\prod_{n=1}^{N}\int d^3\boldsymbol{x}_n\,|\boldsymbol{x}_n,t_n\rangle\langle\boldsymbol{x}_n,t_n|\right)|\psi\rangle \\ &= \int d^3\boldsymbol{x}_N\ldots\int d^3\boldsymbol{x}_1\langle\boldsymbol{x}|U(t,t_N)|\boldsymbol{x}_N\rangle\langle\boldsymbol{x}_N|U(t_N,t_{N-1})|\boldsymbol{x}_{N-1}\rangle\ldots \\ &\quad\times\langle\boldsymbol{x}_2|U(t_2,t_1)|\boldsymbol{x}_1\rangle\langle\boldsymbol{x}_1|U(t_1,t_0)|\psi\rangle.\end{aligned} \tag{14.4}$$

Equivalently, we could also have arrived at this equation directly from the composition property (13.5) of the time evolution operator and the completeness of the Schrödinger picture eigenkets $|\boldsymbol{x}\rangle$.
Equation (14.4) implies in particular for the initial state $|\psi(t_0)\rangle = |\boldsymbol{x}_0\rangle \equiv |\boldsymbol{x}_0, t_0\rangle$ the evolution equation

$$\begin{aligned}\langle \boldsymbol{x}, t|\boldsymbol{x}_0\rangle &= \langle \boldsymbol{x}|U(t,t_0)|\boldsymbol{x}_0\rangle \\ &= \int d^3\boldsymbol{x}_N \ldots \int d^3\boldsymbol{x}_1 \langle \boldsymbol{x}|U(t,t_N)|\boldsymbol{x}_N\rangle\langle \boldsymbol{x}_N|U(t_N,t_{N-1})|\boldsymbol{x}_{N-1}\rangle \ldots \\ &\quad \times \langle \boldsymbol{x}_2|U(t_2,t_1)|\boldsymbol{x}_1\rangle\langle \boldsymbol{x}_1|U(t_1,t_0)|\boldsymbol{x}_0\rangle. \end{aligned} \tag{14.5}$$

Intuitively the formula (14.5) can be considered as an integration over the set of all paths that a particle can take from an initial location $\boldsymbol{x}_0$ at time t_0 to the location $\boldsymbol{x}$ at time t. In particular, if we use

$$\begin{aligned}\langle \boldsymbol{x}|U(t,t_0)|\boldsymbol{x}_0\rangle &= \langle \boldsymbol{x}| \exp\left[-\mathrm{i}\frac{t-t_0}{\hbar}\left(\frac{\mathbf{p}^2}{2m}+V(\mathbf{x})\right)\right]|\boldsymbol{x}_0\rangle \\ &= \langle \boldsymbol{x}| \lim_{N\to\infty}\left[1-\mathrm{i}\frac{t-t_0}{N\hbar}\left(\frac{\mathbf{p}^2}{2m}+V(\mathbf{x})\right)\right]^N |\boldsymbol{x}_0\rangle \end{aligned} \tag{14.6}$$

and substitute the following peculiar decomposition of unity,

$$\begin{aligned}1 &= \int d^3\boldsymbol{x} \int d^3\boldsymbol{p}\, |\boldsymbol{x}\rangle\langle \boldsymbol{x}|\boldsymbol{p}\rangle\langle \boldsymbol{p}| \\ &= \int d^3\boldsymbol{x} \int \frac{d^3\boldsymbol{p}}{\sqrt{2\pi\hbar}^3}\, |\boldsymbol{x}\rangle \exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{p}\cdot\boldsymbol{x}\right)\langle \boldsymbol{p}| \end{aligned} \tag{14.7}$$

between any two factors in the product (14.6), we find

$$\begin{aligned}\langle \boldsymbol{x}, t|\boldsymbol{x}_0\rangle &= \langle \boldsymbol{x}|U(t,t_0)|\boldsymbol{x}_0\rangle \\ &= \lim_{N\to\infty}\left(\prod_{I=1}^{N}\int \frac{d^3\boldsymbol{x}_I d^3\boldsymbol{p}_I}{\sqrt{2\pi\hbar}^3}\right)\exp\left(\frac{\mathrm{i}}{\hbar}\sum_{J=1}^{N}\boldsymbol{p}_J\cdot\boldsymbol{x}_J\right)\langle \boldsymbol{x}|\boldsymbol{x}_N\rangle\langle \boldsymbol{p}_N| \\ &\quad \times\left[1-\mathrm{i}\frac{t-t_0}{N\hbar}\left(\frac{\mathbf{p}^2}{2m}+V(\mathbf{x})\right)\right]|\boldsymbol{x}_{N-1}\rangle\langle \boldsymbol{p}_{N-1}|\ldots \\ &\quad \times|\boldsymbol{x}_2\rangle\langle \boldsymbol{p}_2|\left[1-\mathrm{i}\frac{t-t_0}{N\hbar}\left(\frac{\mathbf{p}^2}{2m}+V(\mathbf{x})\right)\right]|\boldsymbol{x}_1\rangle\langle \boldsymbol{p}_1| \\ &\quad \times\left[1-\mathrm{i}\frac{t-t_0}{N\hbar}\left(\frac{\mathbf{p}^2}{2m}+V(\mathbf{x})\right)\right]|\boldsymbol{x}_0\rangle. \end{aligned} \tag{14.8}$$

The momentum integrals are

$$\begin{aligned}&\int \frac{d^3\boldsymbol{p}_I}{\sqrt{2\pi\hbar}^3}\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{p}_I\cdot\boldsymbol{x}_I\right)\langle \boldsymbol{p}_N|\left[1-\mathrm{i}\frac{t-t_0}{N\hbar}\left(\frac{\mathbf{p}^2}{2m}+V(\mathbf{x})\right)\right]|\boldsymbol{x}_{I-1}\rangle \\ &= \int \frac{d^3\boldsymbol{p}_I}{(2\pi\hbar)^3}\left[1-\mathrm{i}\frac{t-t_0}{N\hbar}\left(V(\boldsymbol{x}_{I-1})-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\boldsymbol{x}_{I-1}^2}\right)\right]\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{p}_I\cdot(\boldsymbol{x}_I-\boldsymbol{x}_{I-1})\right) \\ &= \left[1-\mathrm{i}\frac{t-t_0}{N\hbar}\left(V(\boldsymbol{x}_{I-1})-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\boldsymbol{x}_{I-1}^2}\right)\right]\delta(\boldsymbol{x}_I-\boldsymbol{x}_{I-1}), \end{aligned} \tag{14.9}$$

and this exactly returns equation (14.6) if we would have substituted N copies of

$$1 = \int d^3\boldsymbol{x}\, |\boldsymbol{x}\rangle\langle\boldsymbol{x}|$$

instead of (14.7). This is exactly as it should be. However, if we instead substitute

$$\left[1 - \mathrm{i}\frac{t-t_0}{N\hbar}\left(\frac{\boldsymbol{p}_I^2}{2m} + V(\boldsymbol{x}_{I-1})\right)\right] \simeq \exp\left[-\mathrm{i}\frac{t-t_0}{N\hbar}\left(\frac{\boldsymbol{p}_I^2}{2m} + V(\boldsymbol{x}_{I-1})\right)\right]$$

in (14.9), we find that the momentum integrals are

$$\begin{aligned}
&\int \frac{d^3\boldsymbol{p}_I}{(2\pi\hbar)^3}\, \exp\left[-\mathrm{i}\frac{t-t_0-\mathrm{i}\epsilon}{2m\hbar N}\left(\boldsymbol{p}_I - mN\frac{\boldsymbol{x}_I - \boldsymbol{x}_{I-1}}{t-t_0-\mathrm{i}\epsilon}\right)^2\right] \\
&\quad \times \exp\left(\mathrm{i}N\frac{m}{2\hbar}\frac{(\boldsymbol{x}_I - \boldsymbol{x}_{I-1})^2}{t-t_0}\right) \\
&= \sqrt{\frac{mN}{2\pi\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}}^{3}\, \exp\left[\frac{\mathrm{i}}{\hbar}\frac{m}{2}\left(N\frac{\boldsymbol{x}_I - \boldsymbol{x}_{I-1}}{t-t_0}\right)^2 \frac{t-t_0}{N}\right].
\end{aligned}$$

This motivates the following formula for the matrix elements of the time evolution operator,

$$\begin{aligned}
\langle\boldsymbol{x}, t|\boldsymbol{x}_0\rangle &= \langle\boldsymbol{x}|U(t,t_0)|\boldsymbol{x}_0\rangle \\
&\simeq \lim_{N\to\infty} \sqrt{\frac{mN}{2\pi\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}}^{3N} \left(\prod_{I=1}^{N}\int d^3\boldsymbol{x}_I\right)\delta(\boldsymbol{x}-\boldsymbol{x}_N) \qquad (14.10)\\
&\quad \times \exp\left(\frac{\mathrm{i}}{\hbar}\sum_{J=1}^{N}\left[\frac{m}{2}\left(N\frac{\boldsymbol{x}_I - \boldsymbol{x}_{I-1}}{t-t_0}\right)^2 - V(\boldsymbol{x}_{J-1})\right]\frac{t-t_0}{N}\right).
\end{aligned}$$

The exponent is a discretized version of the action integral of a non-relativistic particle, and this motivates the further short hand notation

$$\begin{aligned}
\langle\boldsymbol{x}|U(t,t_0)|\boldsymbol{x}_0\rangle &= \int_{\boldsymbol{x}(t_0)=\boldsymbol{x}_0}^{\boldsymbol{x}(t)=\boldsymbol{x}} D^3\boldsymbol{x}(t')\, \exp\left[\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} dt'\, \left(\frac{m}{2}\dot{\boldsymbol{x}}^2(t') - V(\boldsymbol{x}(t'))\right)\right] \\
&= \int_{\boldsymbol{x}(t_0)=\boldsymbol{x}_0}^{\boldsymbol{x}(t)=\boldsymbol{x}} D^3\boldsymbol{x}(t')\, \exp\left(\frac{\mathrm{i}}{\hbar}S[\boldsymbol{x}(t')]\right), \qquad (14.11)
\end{aligned}$$

where $S[\boldsymbol{x}(t')]$ is the action functional of the particle (see Appendix A). Please note that this standard notation for path integrals is misleading with regard to the length dimension or units of the path integral. The $\boldsymbol{x}$ matrix elements of the time evolution operator have dimension length^{-3} in agreement with the dimension length$^{-3/2}$ of $\mathbf{x}$ eigenstates in three dimensions, see Section 5.3. This of course agrees with the discretized version on the right hand side of equation (14.11). The three-dimensional path integral therefore has dimension length^{-3},

but the notation $\int D^3\boldsymbol{x}\exp(\mathrm{i}S[\boldsymbol{x}]/\hbar)$ suggests length dimension length^3. A dimensionally correct, but also more awkward notation would be

$$\langle \boldsymbol{x}|U(t,t_0)|\boldsymbol{x}_0\rangle = \delta\big(\boldsymbol{x}(t_0)-\boldsymbol{x}_0\big)\delta\big(\boldsymbol{x}(t)-\boldsymbol{x}\big) \times \int D^3\boldsymbol{x}(t')\,\exp\left(\frac{\mathrm{i}}{\hbar}S[\boldsymbol{x}(t')]\right), \tag{14.12}$$

where the end point integration of the path would implement the boundary point constraints. We will continue to use the standard notation (14.11), but keep the fact in mind that this notation is not dimensionally correct.

Equation (14.11) defines the path integral representation of the propagator in configuration ($\boldsymbol{x}$) space. Note that nothing in the derivation required forward evolution $t > t_0$ in time. Of course, the same results apply for backward evolution. However, the discretization into time steps $(t-t_0)/N$ imply that consecutive steps are either always later or always earlier depending on $t > t_0$ or $t < t_0$, respectively. Therefore path integrals with factors like $\boldsymbol{x}(t_1)\boldsymbol{x}(t_2)$ in the integrand correpond to time ordered matrix elements in canonical quantization, but whether time ordering refers to later times or earlier times depends on whether we are studying forward or backward evolution in time. Usually we are interested in forward evolution, i.e. we assume $t > t_0$ in the following.

A virtue of the path integral is that it explains the principle of stationary action of classical paths as a consequence of dominant contributions from those trajectories where small fluctuations of the path do not yield cancellation of the integral from phase fluctuations.

As a relatively simple exercise, let us see how this reproduces the $\boldsymbol{x}$ representation (4.37) of the free propagator.

The integrations in (14.11) for $V(\boldsymbol{x}) = 0$ include a set of $N-1$ Gaussian integrals. The first integral over $d^3\boldsymbol{x}_1$ yields

$$\begin{aligned}
&\sqrt{\frac{mN}{2\pi\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}}^{3}\ \exp\left[-\frac{mN}{2\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}\frac{1}{2}\left(\boldsymbol{x}_2-\boldsymbol{x}_0\right)^2\right] \\
&\quad\times\int d^3\boldsymbol{x}_1\,\exp\left[-\frac{mN}{2\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}2\left(\boldsymbol{x}_1-\frac{\boldsymbol{x}_2+\boldsymbol{x}_0}{2}\right)^2\right] \\
&= \frac{1}{\sqrt{2}^3}\exp\left[-\frac{mN}{2\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}\frac{1}{2}\left(\boldsymbol{x}_2-\boldsymbol{x}_0\right)^2\right].
\end{aligned}$$

Next we evaluate the $\boldsymbol{x}_2$ integral and then work consecutively through all the integrals. This reproduces always a similar result with minor variations. One

can show by induction with respect to I that the $\boldsymbol{x}_I$ integral yields

$$\begin{aligned}
&\sqrt{\frac{mN}{2\pi\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)I}}^{3} \exp\left[-\frac{mN}{2\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}\frac{1}{I+1}\left(\boldsymbol{x}_{I+1}-\boldsymbol{x}_0\right)^2\right] \\
&\quad\times\int d^3\boldsymbol{x}_I \exp\left[-\frac{mN}{2\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}\frac{I+1}{I}\left(\boldsymbol{x}_I-\frac{I}{I+1}\left(\boldsymbol{x}_{I+1}+\frac{\boldsymbol{x}_0}{I}\right)\right)^2\right] \\
&= \frac{1}{\sqrt{I+1}^3}\exp\left[-\frac{mN}{2\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}\frac{1}{I+1}\left(\boldsymbol{x}_{I+1}-\boldsymbol{x}_0\right)^2\right].
\end{aligned}$$

After the final integrations over $\boldsymbol{x}_{N-1}$ and $\boldsymbol{x}_N$ (which is trivial due to the δ function in (14.11)), we are left with

$$\begin{aligned}
\langle\boldsymbol{x},t|\boldsymbol{x}_0\rangle &= \langle\boldsymbol{x}|U(t,t_0)|\boldsymbol{x}_0\rangle \\
&= \sqrt{\frac{m}{2\pi\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}}^{3}\exp\left[-\frac{m\left(\boldsymbol{x}-\boldsymbol{x}_0\right)^2}{2\mathrm{i}\hbar(t-t_0-\mathrm{i}\epsilon)}\right],
\end{aligned}$$

which is indeed the $\boldsymbol{x}$ representation (4.37) of the free propagator.
Note that the classical trajectory of the particle from the location $\boldsymbol{x}_0$ at time t_0 to the location $\boldsymbol{x}$ at time t is given by

$$\boldsymbol{x}_{cl}(t') = \boldsymbol{x}_0 + \frac{\boldsymbol{x}-\boldsymbol{x}_0}{t-t_0}(t'-t_0) = \boldsymbol{x}\frac{t'-t_0}{t-t_0} + \boldsymbol{x}_0\frac{t'-t}{t_0-t},$$

and therefore the factor in the exponent of the free propagator is just the action functional evaluated on the classical trajectory,

$$\frac{m}{2}\frac{\left(\boldsymbol{x}-\boldsymbol{x}_0\right)^2}{t-t_0} = S[\boldsymbol{x}_{cl}(t')].$$

This holds in general for propagators where the Lagrange function contains at most second order terms in particle velocities and locations, and the path integral formulation is particularly well suited to prove this. If the Lagrange function contains at most second order terms in $\dot{\boldsymbol{x}}$ and $\boldsymbol{x}$, then due to fixed initial and final points $\boldsymbol{x}(t_0)\equiv\boldsymbol{x}_0$ and $\boldsymbol{x}(t)\equiv\boldsymbol{x}$, the action functional for all admissible paths $\boldsymbol{x}(t')$ is exactly

$$\begin{aligned}
S[\boldsymbol{x}(t')] = S[\boldsymbol{x}_{cl}(t')] &+ \frac{1}{2}\int_{t_0}^{t}dt''\int_{t_0}^{t}dt'\left(\boldsymbol{x}(t'')-\boldsymbol{x}_{cl}(t'')\right) \\
&\times\frac{\delta^2 S}{\delta\boldsymbol{x}(t'')\delta\boldsymbol{x}(t')}\cdot\left(\boldsymbol{x}(t')-\boldsymbol{x}_{cl}(t')\right),
\end{aligned} \tag{14.13}$$

see Problem 1. Functional integration over $\exp(\mathrm{i}S[\boldsymbol{x}(t')]/\hbar)$ then yields a constant from the Gaussian integral over the fluctuations $\boldsymbol{x}(t')-\boldsymbol{x}_{cl}(t')$, and a remnant exponential factor,

$$\langle\boldsymbol{x}|U(t,t_0)|\boldsymbol{x}_0\rangle \sim \exp\left(\frac{\mathrm{i}}{\hbar}S[\boldsymbol{x}_{cl}(t')]\right).$$

14.2 Path integrals in scattering theory

We have seen in Chapter 13 that the calculation of transition probabilities or scattering cross section from an initial state $|\psi_i(t')\rangle$ to a final state $|\psi_f(t)\rangle$ requires the calculation of the scattering matrix element

$$S_{fi}(t,t') = \langle\psi_f(t)|U(t,t')|\psi_i(t')\rangle = \langle\psi_f|U_D(t,t')|\psi_i\rangle,$$

where

$$U_D(t,t') = \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau\,H(\tau)\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t'\right)$$

is the time evolution operator on the states in the interaction picture. We also recall that the usual default definition of the scattering matrix involves $t\to\infty$, $t'\to-\infty$, $S_{fi}\equiv S_{fi}(\infty,-\infty)$. For the following discussion it is convenient to relabel initial and final times as $t'\to t_i$, $t\to t_f$. Equation (14.11) then implies a connection between scattering matrix elements and path integrals,

$$\begin{aligned}S_{fi} = &\lim_{t_i\to-\infty,t_f\to\infty}\int d^3\boldsymbol{x}_f\int d^3\boldsymbol{x}_i\,\langle\psi_f|\exp\left(\frac{\mathrm{i}}{\hbar}H_0 t_f\right)|\boldsymbol{x}_f\rangle\\ &\times\int_{\boldsymbol{x}(t_i)=\boldsymbol{x}_i}^{\boldsymbol{x}(t_f)=\boldsymbol{x}_f}D^3\boldsymbol{x}(t)\,\exp\left(\frac{\mathrm{i}}{\hbar}S[\boldsymbol{x}(t)]\right)\langle\boldsymbol{x}_i|\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t_i\right)|\psi_i\rangle.\end{aligned}\tag{14.14}$$

This is still a mixed formula involving both canonical operators and a path integral. We now assume that our initial and final states are momentum eigenstates $|\psi_i\rangle = |\boldsymbol{p}_i\rangle$ and $|\psi_f\rangle = |\boldsymbol{p}_f\rangle$, and we also assume that the scattering potential $V(\boldsymbol{x},t)$ is localized with finite range. The free Hamiltonian for the free-free scattering problem is $H_0 = \mathbf{p}^2/2m$. The resulting scattering matrix element is then

$$\begin{aligned}S_{fi} = &\lim_{t_i\to-\infty,t_f\to\infty}\int d^3\boldsymbol{x}_f\int d^3\boldsymbol{x}_i\int_{\boldsymbol{x}(t_i)=\boldsymbol{x}_i}^{\boldsymbol{x}(t_f)=\boldsymbol{x}_f}D^3\boldsymbol{x}(t)\,\exp\left(\frac{\mathrm{i}}{\hbar}S[\boldsymbol{x}(t)]\right)\\ &\times\frac{1}{(2\pi\hbar)^3}\exp\left[\frac{\mathrm{i}}{\hbar}\left(\frac{\boldsymbol{p}_f^2 t_f-\boldsymbol{p}_i^2 t_i}{2m}+\boldsymbol{p}_i\cdot\boldsymbol{x}_i-\boldsymbol{p}_f\cdot\boldsymbol{x}_f\right)\right].\end{aligned}\tag{14.15}$$

For the perturbative evaluation of (14.15) we introduce an auxiliary external force $\boldsymbol{F}(t)$, such that the Lagrange function including the scattering potential $V(\boldsymbol{x},t)$ takes the form

$$L = \frac{m}{2}\dot{\boldsymbol{x}}^2(t) - V(\boldsymbol{x}(t),t) + \boldsymbol{F}(t)\cdot\boldsymbol{x}(t).$$

The path integral in (14.15) then takes the form

$$\begin{aligned}
&\int D^3\boldsymbol{x}(t)\,\exp\!\left(\frac{\mathrm{i}}{\hbar}S[\boldsymbol{x}(t)]\right) = \int D^3\boldsymbol{x}(t)\,\sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n n!}\int_{t_i}^{t_f}dt_1\ldots\int_{t_i}^{t_f}dt_n \\
&\quad\times V(\boldsymbol{x}(t_1),t_1)\ldots V(\boldsymbol{x}(t_n),t_n)\exp\!\left[\frac{\mathrm{i}}{\hbar}\int_{t_i}^{t_f}dt\left(\frac{m}{2}\dot{\boldsymbol{x}}^2(t)+\boldsymbol{F}(t)\cdot\boldsymbol{x}(t)\right)\right] \\
&= \int D^3\boldsymbol{x}(t)\,\sum_{n=0}^{\infty}\frac{1}{(\mathrm{i}\hbar)^n n!}\int_{t_i}^{t_f}dt_1\ldots\int_{t_i}^{t_f}dt_n\,V\!\left(-\mathrm{i}\hbar\frac{\delta}{\delta\boldsymbol{F}(t_1)},t_1\right)\ldots \\
&\quad\times V\!\left(-\mathrm{i}\hbar\frac{\delta}{\delta\boldsymbol{F}(t_n)},t_n\right)\exp\!\left[\frac{\mathrm{i}}{\hbar}\int_{t_i}^{t_f}dt\left(\frac{m}{2}\dot{\boldsymbol{x}}^2(t)+\boldsymbol{F}(t)\cdot\boldsymbol{x}(t)\right)\right] \\
&= \int D^3\boldsymbol{x}(t)\,\exp\!\left[-\frac{\mathrm{i}}{\hbar}\int_{t_i}^{t_f}dt'\,V\!\left(-\mathrm{i}\hbar\frac{\delta}{\delta\boldsymbol{F}(t')},t'\right)\right] \\
&\quad\times\exp\!\left[\frac{\mathrm{i}}{\hbar}\int_{t_i}^{t_f}dt\left(\frac{m}{2}\dot{\boldsymbol{x}}^2(t)+\boldsymbol{F}(t)\cdot\boldsymbol{x}(t)\right)\right]. \qquad (14.16)
\end{aligned}$$

Evaluation of the Gaussian integrals as in equation (14.11) for $V(\boldsymbol{x}) = 0$ reproduces the canonical perturbation series (13.13). However, a different representation is gotten if we pull the variational derivative operators $V(-\mathrm{i}\hbar[\delta/\delta\boldsymbol{F}(t)],t)$ out of the path integral,

$$\int D^3\boldsymbol{x}(t)\,\exp\!\left(\frac{\mathrm{i}}{\hbar}S[\boldsymbol{x}(t)]\right) = \exp\!\left[-\frac{\mathrm{i}}{\hbar}\int_{t_i}^{t_f}dt'\,V\!\left(-\mathrm{i}\hbar\frac{\delta}{\delta\boldsymbol{F}(t')},t'\right)\right]Z[\boldsymbol{F}],$$

$$Z[\boldsymbol{F}] = \int D^3\boldsymbol{x}(t)\,\exp\!\left[\frac{\mathrm{i}}{\hbar}\int_{t_i}^{t_f}dt\left(\frac{m}{2}\dot{\boldsymbol{x}}^2(t)+\boldsymbol{F}(t)\cdot\boldsymbol{x}(t)\right)\right]. \qquad (14.17)$$

This swapping of the variational derivative operators with the integration over paths is a corner stone of applications of path integrals in perturbative field theory, but it is a very delicate point because inclusion of the potential terms within the path integral implies automatic time ordering of the potential terms, due to the evaluation of path integrals in small time steps. This time ordering of the potential terms is generically lost if we evaluate the reduced path integral (14.17) first and perform the variational derivatives $\delta/\delta\boldsymbol{F}(t)$ afterwards only on the resulting functional $Z[\boldsymbol{F}]$, because the classical variational operators commute,

$$\frac{\delta}{\delta\boldsymbol{F}(t)}\otimes\frac{\delta}{\delta\boldsymbol{F}(t')} = \frac{\delta}{\delta\boldsymbol{F}(t')}\otimes\frac{\delta}{\delta\boldsymbol{F}(t)}.$$

Fortunately, this problem is cured through inherent time ordering in the Green's function appearing in $Z[\boldsymbol{F}]$, if this Green's function is determined in such a way that the expression $-\hbar^2\delta^2 Z[\boldsymbol{F}]/(\delta\boldsymbol{F}(t)\otimes\delta\boldsymbol{F}(t'))$ matches the two-point function $\langle\boldsymbol{x}_f,t_f|\mathbf{x}(t)\otimes\mathbf{x}(t')|\boldsymbol{x}_i,t_i\rangle$ of the canonical theory for $t_f > t > t' > t_i$. Therefore we will continue with the evaluation of the path integral $Z[\boldsymbol{F}]$.

The equation of motion of a classical non-relativistic particle under the influence of a force $\boldsymbol{F}(t)$ is directly integrable,

$$\boldsymbol{x}(t) = \boldsymbol{x}_i + \boldsymbol{v}_i(t-t_i) + \frac{1}{m}\int_{t_i}^{t} dt' \int_{t_i}^{t'} dt''\, \boldsymbol{F}(t''). \tag{14.18}$$

Partial integration of the acceleration term yields a Green's function representation

$$\begin{aligned}\boldsymbol{x}(t) &= \boldsymbol{x}_i + \boldsymbol{v}_i(t-t_i) + \frac{1}{m}\int_{t_i}^{t} dt'\,(t-t')\boldsymbol{F}(t') \\ &= \boldsymbol{x}_i + \boldsymbol{v}_i(t-t_i) + \frac{1}{m}\int_{-\infty}^{\infty} dt'\, G_i(t,t')\boldsymbol{F}(t'),\end{aligned} \tag{14.19}$$

with a Green's function which satisfies homogeneous initial conditions,

$$\begin{aligned}G_i(t,t') &= (t-t')\left[\Theta(t-t') - \Theta(t_i-t')\right] \\ &= (t-t')\left[\Theta(t'-t_i) - \Theta(t'-t)\right],\end{aligned} \tag{14.20}$$

$$\frac{\partial^2}{\partial t^2}G_i(t,t') = \delta(t-t'), \quad \frac{\partial}{\partial t}G_i(t,t')\bigg|_{t=t_i} = 0, \quad G_i(t_i,t') = 0.$$

If we determine the velocity $\boldsymbol{v}_i$ such that $\boldsymbol{x}(t_f) = \boldsymbol{x}_f$, we find another Green's function representation

$$\begin{aligned}\boldsymbol{x}(t) &= \boldsymbol{x}_i\frac{t-t_f}{t_i-t_f} + \boldsymbol{x}_f\frac{t-t_i}{t_f-t_i} + \int_{t_f}^{t} dt'\,\frac{tt_f+t't_i}{t_f-t_i}\frac{\boldsymbol{F}(t')}{m} \\ &\quad + \int_{t_i}^{t} dt'\,\frac{tt_i+t't_f}{t_i-t_f}\frac{\boldsymbol{F}(t')}{m} + \int_{t_i}^{t_f} dt'\,\frac{tt'+t_it_f}{t_f-t_i}\frac{\boldsymbol{F}(t')}{m} \\ &= \boldsymbol{x}_i\frac{t-t_f}{t_i-t_f} + \boldsymbol{x}_f\frac{t-t_i}{t_f-t_i} + \frac{1}{m}\int_{-\infty}^{\infty} dt'\, G_{fi}(t,t')\boldsymbol{F}(t'),\end{aligned} \tag{14.21}$$

with a Green's function which satisfies homogeneous boundary conditions,

$$\begin{aligned}G_{fi}(t,t') = &\frac{tt_f+t't_i}{t_f-t_i}\left[\Theta(t-t') - \Theta(t_f-t')\right] \\ &+\frac{tt_i+t't_f}{t_i-t_f}\left[\Theta(t-t') - \Theta(t_i-t')\right] \\ &+\frac{tt'+t_it_f}{t_f-t_i}\left[\Theta(t_f-t') - \Theta(t_i-t')\right],\end{aligned} \tag{14.22}$$

$$\frac{\partial^2}{\partial t^2}G_{fi}(t,t') = \delta(t-t'), \quad G_{fi}(t_f,t') = 0, \quad G_{fi}(t_i,t') = 0.$$

The most general form of the Green's function for the Newton equation is

$$G(t,t') = \frac{|t-t'|}{2} + \alpha(t')t + \beta(t'). \tag{14.23}$$

It is useful to have a convolution notation for the following calculations. We define

$$(G \circ \boldsymbol{F})(t) \equiv \int_{-\infty}^{\infty} dt'\, G(t,t')\boldsymbol{F}(t')$$

and

$$(\dot{G} \circ \boldsymbol{F})(t) \equiv \int_{-\infty}^{\infty} dt'\, \frac{\partial}{\partial t} G(t,t')\boldsymbol{F}(t').$$

Partial integration yields the following representation of the action of a particle under the influence of a force $\boldsymbol{F}(t)$ for every Green's function (14.23),

$$\begin{aligned}\int_{t_i}^{t_f} dt \left(\frac{m}{2}\dot{\boldsymbol{x}}^2(t) + \boldsymbol{F}(t)\cdot\boldsymbol{x}(t)\right) &= \left(\boldsymbol{x}(t_f) - \frac{(G\circ\boldsymbol{F})(t_f)}{2m}\right)\cdot(\dot{G}\circ\boldsymbol{F})(t_f)\\ &- \left(\boldsymbol{x}(t_i) - \frac{(G\circ\boldsymbol{F})(t_i)}{2m}\right)\cdot(\dot{G}\circ\boldsymbol{F})(t_i)\\ &+\frac{m}{2}\int_{t_i}^{t_f} dt \left(\dot{\boldsymbol{x}}(t) - \frac{(\dot{G}\circ\boldsymbol{F})(t)}{m}\right)^2 + \frac{1}{2m}\int_{t_i}^{t_f} dt\, \boldsymbol{F}(t)\cdot(G\circ\boldsymbol{F})(t). \qquad (14.24)\end{aligned}$$

The trajectory $\boldsymbol{x}(t)$ between $\boldsymbol{x}_i$ and $\boldsymbol{x}_f$ appears only in the free particle action for the free trajectory

$$\boldsymbol{X}(t) = \boldsymbol{x}(t) - \frac{1}{m}(G\circ\boldsymbol{F})(t), \qquad (14.25)$$

which classically satisfies $\ddot{\boldsymbol{X}}(t) = \boldsymbol{0}$. Therefore the path integral (14.17) can be evaluated in terms of the result for the free particle,

$$\begin{aligned}Z[\boldsymbol{F}] &= \sqrt{\frac{m}{2\pi \mathrm{i}\hbar(t_f-t_i)}}^{3} \exp\left[\frac{\mathrm{i}}{\hbar}\left(\boldsymbol{X}_f\cdot(\dot{G}\circ\boldsymbol{F})(t_f) - \boldsymbol{X}_i\cdot(\dot{G}\circ\boldsymbol{F})(t_i)\right)\right]\\ &\quad\times\exp\left(\mathrm{i}m\frac{(\boldsymbol{X}_f-\boldsymbol{X}_i)^2}{2\hbar(t_f-t_i)} + \frac{\mathrm{i}}{2m\hbar}\int_{t_i}^{t_f} dt\, \boldsymbol{F}(t)\cdot(G\circ\boldsymbol{F})(t)\right)\\ &= \langle \boldsymbol{X}_f|U_0(t_f,t_i)|\boldsymbol{X}_i\rangle \exp\left(\frac{\mathrm{i}}{2m\hbar}\int_{t_i}^{t_f} dt\, \boldsymbol{F}(t)\cdot(G\circ\boldsymbol{F})(t)\right)\\ &\quad\times\exp\left[\frac{\mathrm{i}}{\hbar}\left(\boldsymbol{X}_f\cdot(\dot{G}\circ\boldsymbol{F})(t_f) - \boldsymbol{X}_i\cdot(\dot{G}\circ\boldsymbol{F})(t_i)\right)\right]. \qquad (14.26)\end{aligned}$$

We can summarize our results in the equations

$$S_{fi} = \lim_{t_i\to-\infty, t_f\to\infty} \exp\left[-\frac{\mathrm{i}}{\hbar}\int_{t_i}^{t_f} dt\, V\left(-\mathrm{i}\hbar\frac{\delta}{\delta\boldsymbol{F}(t)}, t\right)\right] S_{fi}^{(V=0)}, \qquad (14.27)$$

$$\begin{aligned}S_{fi}^{(V=0)} &= \frac{1}{(2\pi\hbar)^3}\int d^3\boldsymbol{X}_f \int d^3\boldsymbol{X}_i\, Z[\boldsymbol{F}](\boldsymbol{X}_f,t_f;\boldsymbol{X}_i,t_i)\\ &\quad\times\exp\left(\mathrm{i}\frac{\boldsymbol{p}_f^2 t_f - \boldsymbol{p}_i^2 t_i}{2m\hbar}\right)\exp\left[\frac{\mathrm{i}}{\hbar}\boldsymbol{p}_i\cdot\left(\boldsymbol{X}_i + \frac{1}{m}(G\circ\boldsymbol{F})(t_i)\right)\right]\\ &\quad\times\exp\left[-\frac{\mathrm{i}}{\hbar}\boldsymbol{p}_f\cdot\left(\boldsymbol{X}_f + \frac{1}{m}(G\circ\boldsymbol{F})(t_f)\right)\right]. \qquad (14.28)\end{aligned}$$

The integrals over $\boldsymbol{X}_f$ and $\boldsymbol{X}_i$ amount to a Gaussian integral involving $\boldsymbol{X}_f - \boldsymbol{X}_i$ and an integral over a Fourier monomial involving $\boldsymbol{X}_i$. Evaluation of the integrals yields

$$\begin{aligned} S_{fi}^{(V=0)} &= \exp\left(\frac{\mathrm{i}}{2m\hbar}\int_{t_i}^{t_f} dt\, \boldsymbol{F}(t)\cdot(G\circ\boldsymbol{F})(t)\right) \\ &\times \exp\left(\frac{\mathrm{i}\boldsymbol{p}_f}{m\hbar}\cdot\left[t_f(\dot{G}\circ\boldsymbol{F})(t_f) - (G\circ\boldsymbol{F})(t_f)\right]\right) \\ &\times \exp\left(-\frac{\mathrm{i}\boldsymbol{p}_i}{m\hbar}\cdot\left[t_i(\dot{G}\circ\boldsymbol{F})(t_i) - (G\circ\boldsymbol{F})(t_i)\right]\right) \\ &\times \delta\Big(\boldsymbol{p}_f - (\dot{G}\circ\boldsymbol{F})(t_f) - \boldsymbol{p}_i + (\dot{G}\circ\boldsymbol{F})(t_i)\Big). \end{aligned} \tag{14.29}$$

For consistency we note that this reproduces the correct result $S_{fi} = \delta(\boldsymbol{p}_f - \boldsymbol{p}_i)$ for the free particle. The δ function implies conservation of the free momentum $\boldsymbol{P} = \boldsymbol{p}(t) - (\dot{G}\circ\boldsymbol{F})(t)$, or equivalently matching of the external momenta under evolution with the force $\boldsymbol{F}(t)$,

$$\boldsymbol{p}_f = \boldsymbol{p}_i + \int_{t_i}^{t_f} dt\, \boldsymbol{F}(t). \tag{14.30}$$

Please note that it is not possible to impose simultaneous boundary conditions

$$t_f\,\frac{\partial}{\partial t}G(t,t')\bigg|_{t=t_f} = G(t_f,t')$$

and

$$t_i\,\frac{\partial}{\partial t}G(t,t')\bigg|_{t=t_i} = G(t_i,t'),$$

because such a Green's function does not exist. As a consequence it is not possible to eliminate the initial and final state dependent exponentials in the scattering matrix through a clever choice of the Green's function. This is of course as it should be, because the scattering amplitude $\tilde{\mathcal{M}}_{fi} = \mathrm{i}(S_{fi} - \delta_{fi})/\delta(\boldsymbol{P}_f - \boldsymbol{P}_i)$ generically must depend on the initial and final states.

So far the derivation did not restrict the choice of the Green's function $G(t,t')$ (14.23). In the next steps we will fix the functions $\alpha(t')$ and $\beta(t')$ such that the free one and two-point functions from variational derivatives of $Z[\boldsymbol{F}]$ match the corresponding matrix elements in the canonical theory.

The calculation of the one-point function from the path integral (14.26) for $t_i < t < t_f$ is complicated by the fact that the generic Green's function (14.23) shifts $\boldsymbol{x}_{f/i}$ to $\boldsymbol{X}_{f/i}$ according to equation (14.25). This implies

$$\begin{aligned} &\langle \boldsymbol{x}_f, t_f | \boldsymbol{x}(t) | \boldsymbol{x}_i, t_i\rangle = -\mathrm{i}\hbar\,\frac{\delta}{\delta\boldsymbol{F}(t)}Z[\boldsymbol{F}]\bigg|_{\boldsymbol{F}=\boldsymbol{0}} = \langle \boldsymbol{x}_f | U_0(t_f,t_i) | \boldsymbol{x}_i\rangle \\ &\times\left(\frac{\boldsymbol{x}_f + \boldsymbol{x}_i}{2} + \alpha(t)\,(\boldsymbol{x}_f - \boldsymbol{x}_i) + m\frac{\delta}{\delta\boldsymbol{F}(t)}\,(\boldsymbol{X}_f - \boldsymbol{X}_i)\cdot\frac{\boldsymbol{x}_f - \boldsymbol{x}_i}{t_f - t_i}\right). \end{aligned}$$

However, we have

$$m\frac{\delta}{\delta \boldsymbol{F}(t)}\left(\boldsymbol{X}_f - \boldsymbol{X}_i\right) = \alpha(t)(t_i - t_f) + t - \frac{t_f + t_i}{2}.$$

and therefore the path integral result for the one-point function does not depend on the gauge functions $\alpha(t')$ and $\beta(t')$,

$$\begin{aligned}\langle \boldsymbol{x}_f, t_f|\boldsymbol{x}(t)|\boldsymbol{x}_i, t_i\rangle &= -\mathrm{i}\hbar\,\frac{\delta}{\delta \boldsymbol{F}(t)} Z[\boldsymbol{F}]\bigg|_{\boldsymbol{F}=\boldsymbol{0}} = \langle \boldsymbol{x}_f|U_0(t_f, t_i)|\boldsymbol{x}_i\rangle \\ &\quad\times\left(\boldsymbol{x}_f\frac{t - t_i}{t_f - t_i} + \boldsymbol{x}_i\frac{t_f - t}{t_f - t_i}\right). \end{aligned} \tag{14.31}$$

The corresponding canonical one-point function is with the Heisenberg operator

$$\mathbf{x}(t) = \exp\left(\frac{\mathrm{i}t}{2m\hbar}\mathbf{p}^2\right)\mathbf{x}\exp\left(-\frac{\mathrm{i}t}{2m\hbar}\mathbf{p}^2\right) = \mathbf{x} + \frac{t}{m}\mathbf{p}$$

given by

$$\begin{aligned}\langle \boldsymbol{x}_f, t_f|\mathbf{x}(t)|\boldsymbol{x}_i, t_i\rangle &= \langle \boldsymbol{x}_f|\exp\left(-\frac{\mathrm{i}t_f}{2m\hbar}\mathbf{p}^2\right)\left(\mathbf{x} + \frac{t}{m}\mathbf{p}\right)\exp\left(\frac{\mathrm{i}t_i}{2m\hbar}\mathbf{p}^2\right)|\boldsymbol{x}_i\rangle \\ &= \langle \boldsymbol{x}_f|\exp\left(-\mathrm{i}\frac{t_f - t_i}{2m\hbar}\mathbf{p}^2\right)\left(\mathbf{x} + \frac{t - t_i}{m}\mathbf{p}\right)|\boldsymbol{x}_i\rangle \\ &= \left(\boldsymbol{x}_i - \frac{\mathrm{i}\hbar}{m}(t - t_i)\frac{\partial}{\partial \boldsymbol{x}_f}\right)\langle \boldsymbol{x}_f|U_0(t_f, t_i)|\boldsymbol{x}_i\rangle \\ &= \left(\boldsymbol{x}_i + (\boldsymbol{x}_f - \boldsymbol{x}_i)\,\frac{t - t_i}{t_f - t_i}\right)\langle \boldsymbol{x}_f|U_0(t_f, t_i)|\boldsymbol{x}_i\rangle, \end{aligned} \tag{14.32}$$

i.e. the same result that we found in the path integral calculation. The one-point function $\langle \boldsymbol{x}_f, t_f|\boldsymbol{x}(t)|\boldsymbol{x}_i, t_i\rangle$ is fully compatible between the path integral and the canonical formalism and does not restrict the choice of the Green's function in (14.26).

The time ordered canonical two-point function for $t_i < t_1 < t_2 < t_f$ is

$$\begin{aligned}&\langle \boldsymbol{x}_f, t_f|\mathrm{T}\mathbf{x}(t_1)\otimes\mathbf{x}(t_2)|\boldsymbol{x}_i, t_i\rangle = \langle \boldsymbol{x}_f, t_f|\mathbf{x}(t_2)\otimes\mathbf{x}(t_1)|\boldsymbol{x}_i, t_i\rangle \\ &= \langle \boldsymbol{x}_f|\exp\left(-\frac{\mathrm{i}t_f}{2m\hbar}\mathbf{p}^2\right)\left(\mathbf{x} + \frac{t_2}{m}\mathbf{p}\right)\otimes\left(\mathbf{x} + \frac{t_1}{m}\mathbf{p}\right)\exp\left(\frac{\mathrm{i}t_i}{2m\hbar}\mathbf{p}^2\right)|\boldsymbol{x}_i\rangle \\ &= \langle \boldsymbol{x}_f|\left(\mathbf{x} + \frac{t_2 - t_f}{m}\mathbf{p}\right)\exp\left(-\mathrm{i}\frac{t_f - t_i}{2m\hbar}\mathbf{p}^2\right)\otimes\left(\mathbf{x} + \frac{t_1 - t_i}{m}\mathbf{p}\right)|\boldsymbol{x}_i\rangle \\ &= \left(\boldsymbol{x}_f - \frac{\mathrm{i}\hbar}{m}(t_2 - t_f)\frac{\partial}{\partial \boldsymbol{x}_f}\right)\otimes\left(\boldsymbol{x}_i - \frac{\mathrm{i}\hbar}{m}(t_1 - t_i)\frac{\partial}{\partial \boldsymbol{x}_f}\right)\langle \boldsymbol{x}_f|U_0(t_f, t_i)|\boldsymbol{x}_i\rangle \\ &= \left(\boldsymbol{x}_f + (\boldsymbol{x}_f - \boldsymbol{x}_i)\frac{t_2 - t_f}{t_f - t_i}\right)\otimes\left(\boldsymbol{x}_i + (\boldsymbol{x}_f - \boldsymbol{x}_i)\frac{t_1 - t_i}{t_f - t_i}\right)\langle \boldsymbol{x}_f|U_0(t_f, t_i)|\boldsymbol{x}_i\rangle \\ &\quad -\frac{\mathrm{i}\hbar}{m}\frac{(t_2 - t_f)(t_1 - t_i)}{t_f - t_i}\underline{1}\langle \boldsymbol{x}_f|U_0(t_f, t_i)|\boldsymbol{x}_i\rangle. \end{aligned} \tag{14.33}$$

A lengthy but straightforwad calculation shows that this agrees with the path integral expression

$$\langle \boldsymbol{x}_f, t_f | \boldsymbol{x}(t_2) \otimes \boldsymbol{x}(t_1) | \boldsymbol{x}_i, t_i \rangle = -\hbar^2 \left. \frac{\delta^2 Z[\boldsymbol{F}]}{\delta \boldsymbol{F}(t_2) \otimes \delta \boldsymbol{F}(t_1)} \right|_{\boldsymbol{F}=\boldsymbol{0}}$$

if and only if we choose $\alpha(t') = -1/2$ and $\beta(t') = -t'/2$ in (14.23),

$$G(t,t') = \frac{1}{2}(|t-t'| - t - t') = -t\Theta(t'-t) - t'\Theta(t-t'). \tag{14.34}$$

The limit $t_i \to -\infty$, $t_f \to \infty$ in equation (14.29) then yields the following representation of the scattering matrix element,

$$\begin{aligned} S_{fi}^{(V=0)} &= \exp\left(\frac{\mathrm{i}}{2m\hbar} \boldsymbol{F} \circ \underline{G} \circ \boldsymbol{F} \right) \exp\left(\frac{\mathrm{i}\boldsymbol{p}_f}{m\hbar} \cdot \int_{-\infty}^{\infty} dt'\, t' \boldsymbol{F}(t') \right) \\ &\quad \times \delta\left(\boldsymbol{p}_f - \boldsymbol{p}_i - \int_{-\infty}^{\infty} dt\, \boldsymbol{F}(t) \right), \end{aligned} \tag{14.35}$$

with

$$\begin{aligned} \boldsymbol{F} \circ \underline{G} \circ \boldsymbol{F} &= \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt'\, G(t,t') \boldsymbol{F}(t) \cdot \boldsymbol{F}(t') \\ &= -2 \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt'\, t' \boldsymbol{F}(t) \cdot \boldsymbol{F}(t'). \end{aligned}$$

We can also write the result (14.35) in the more symmetric form

$$\begin{aligned} S_{fi}^{(V=0)} &= \exp\left(\frac{\mathrm{i}}{4m\hbar} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt'\, |t-t'| \boldsymbol{F}(t) \cdot \boldsymbol{F}(t') \right) \\ &\quad \times \exp\left(\mathrm{i} \frac{\boldsymbol{p}_f + \boldsymbol{p}_i}{2m\hbar} \cdot \int_{-\infty}^{\infty} dt\, t \boldsymbol{F}(t) \right) \\ &\quad \times \delta\left(\boldsymbol{p}_f - \boldsymbol{p}_i - \int_{-\infty}^{\infty} dt\, \boldsymbol{F}(t) \right). \end{aligned} \tag{14.36}$$

It seems surprising that substitution of (14.36) into equation (14.27) and setting $\boldsymbol{F} = \boldsymbol{0}$ after evaluation of the functional derivatives yields scattering from the potential V. However, equations (14.27,14.36) compare to the practically useful relation (13.13) (or the equivalent relation (14.16)) for the scattering matrix elements like the representation

$$\langle \boldsymbol{x} | U_0(t-t') | \boldsymbol{x}' \rangle = \exp\left(\mathrm{i}\hbar \frac{t - \mathrm{i}\epsilon}{2m} \frac{\partial^2}{\partial \boldsymbol{x}^2} \right) \delta(\boldsymbol{x} - \boldsymbol{x}')$$

for the $\boldsymbol{x}$ matrix elements of the fee time evolution operator compares to the practically more useful representation (4.37).
Recasting the perturbation series in terms of $V(-\mathrm{i}\hbar\delta/\delta \boldsymbol{F}(t), t)$ instead of $V(\boldsymbol{x}, t)$ does not yield a more efficient or practical representation for potential scattering theory. However, recasting interactions in terms of functional derivatives

is useful when interactions are expressed in terms of higher order products of wave functions instead of potentials. Therefore we used the transcription of potential scattering theory in terms of functional derivatives with respect to auxiliary forces as an illustration for functional methods in perturbation theory.

14.3 Problems

14.1 Verify (14.13) for the general second order particle action

$$S[\boldsymbol{x}(t')] = \int_{t_0}^{t} dt' \left(\frac{1}{2}\dot{\boldsymbol{x}}(t') \cdot \underline{M} \cdot \dot{\boldsymbol{x}}(t') + \frac{1}{2}\boldsymbol{x}(t') \cdot \underline{F} \cdot \dot{\boldsymbol{x}}(t') \right.$$
$$\left. -\frac{1}{2}\boldsymbol{x}(t') \cdot \underline{\Omega^2} \cdot \boldsymbol{x}(t') + \boldsymbol{F} \cdot \boldsymbol{x}(t') \right),$$

$$\underline{F}^T = -\underline{F}, \quad \boldsymbol{x}(t_0) = \boldsymbol{x}_0, \quad \boldsymbol{x}(t) = \boldsymbol{x}.$$

14.2 Which exponential factor in the propagator $\langle \boldsymbol{x}|U(t,t_0)|\boldsymbol{x}_0\rangle$ do you find for a harmonic oscillator?

14.3 Derive the particular Green's functions (14.20) and (14.22) from the general form (14.23).

14.4 Calculate the expression

$$\langle \boldsymbol{x}_f, t_f|\boldsymbol{x}(t_2) \otimes \boldsymbol{x}(t_1)|\boldsymbol{x}_i, t_i\rangle = -\hbar^2 \left. \frac{\delta^2 Z[\boldsymbol{F}]}{\delta \boldsymbol{F}(t_2) \otimes \delta \boldsymbol{F}(t_1)} \right|_{\boldsymbol{F}=\boldsymbol{0}}$$

for arbitrary gauge functions $\alpha(t')$ and $\beta(t')$ in the Green's function and verify that we have to chose (14.34).

14.5 Calculate the time ordered three-point function

$$\langle \boldsymbol{x}_f, t_f|\mathbf{x}(t_3) \otimes \mathbf{x}(t_2) \otimes \mathbf{x}(t_1)|\boldsymbol{x}_i, t_i\rangle, \quad t_i < t_1 < t_2 < t_3 < t_f,$$

both in the canonical formalism and in the path integral formalism.

Chapter 15

Coupling to Electromagnetic Fields

Electromagnetism is the most important interaction for the study of atoms, molecules and materials. It determines most of the potentials or perturbation operators V which are studied in practical applications of quantum mechanics, and it also serves as a basic example for the implementation of other, more complicated interactions in quantum mechanics. Therefore the primary objective of the current chapter is to understand how electromagnetic fields are introduced in the Schrödinger equation.

15.1 Electromagnetic couplings

The introduction of electromagnetic fields into the Schrödinger equation for a particle of mass m and electric charge q can be inferred from the description of the particle in classical Lagrangian mechanics.
The Lagrange function for the particle in electromagnetic fields

$$\boldsymbol{E}(\boldsymbol{x},t) = -\boldsymbol{\nabla}\Phi(\boldsymbol{x},t) - \frac{\partial \boldsymbol{A}(\boldsymbol{x},t)}{\partial t}, \quad \boldsymbol{B}(\boldsymbol{x},t) = \boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{x},t)$$

is

$$L = \frac{m}{2}\dot{\boldsymbol{x}}(t)^2 + q\dot{\boldsymbol{x}}(t) \cdot \boldsymbol{A}(\boldsymbol{x}(t),t) - q\Phi(\boldsymbol{x}(t),t). \tag{15.1}$$

Let us check (or review) that equation (15.1) is indeed the correct Lagrange function for the particle. The electromagnetic potentials in the Lagrange function depend on the time t both explicitly and implicitly through the time dependence $\boldsymbol{x}(t)$ of the trajectory of the particle. The time derivative of the conjugate momentum

$$\boldsymbol{p} = \frac{\partial L}{\partial \dot{\boldsymbol{x}}} = m\dot{\boldsymbol{x}} + q\boldsymbol{A} \tag{15.2}$$

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is therefore

$$\frac{d\boldsymbol{p}}{dt} = m\ddot{\boldsymbol{x}} + q\dot{x}_i \frac{\partial \boldsymbol{A}}{\partial x_i} + q\frac{\partial \boldsymbol{A}}{\partial t}.$$

According to the Euler-Lagrange equations (cf. Appendix A), this must equal

$$\frac{\partial L}{\partial \boldsymbol{x}} = q\dot{x}_i \boldsymbol{\nabla} A_i - q\boldsymbol{\nabla}\Phi.$$

The property (7.12) of the ϵ tensor implies

$$\boldsymbol{e}_i \left(\dot{x}_j \partial_i A_j - \dot{x}_j \partial_j A_i\right) = \boldsymbol{e}_i \epsilon_{ijk}\epsilon_{klm}\dot{x}_j \partial_l A_m = \dot{\boldsymbol{x}} \times \boldsymbol{B},$$

and therefore the Euler-Lagrange equation yields the Lorentz force law

$$m\ddot{\boldsymbol{x}} = q(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B}), \tag{15.3}$$

as required.
The classical Hamiltonian for the particle follows as

$$H = \boldsymbol{p}\cdot\dot{\boldsymbol{x}} - L = \frac{1}{2m}(\boldsymbol{p} - q\boldsymbol{A})^2 + q\Phi = \frac{m}{2}\dot{\boldsymbol{x}}^2 + q\Phi. \tag{15.4}$$

For the translation of the previous observations into quantum mechanics in $\boldsymbol{x}$-representation, we observe that the substitution

$$m\dot{\boldsymbol{x}} = \boldsymbol{p} \to m\dot{\boldsymbol{x}} = \boldsymbol{p} - q\boldsymbol{A}$$

in the $\boldsymbol{x}$-representation of quantum mechanics corresponds to

$$-\mathrm{i}\hbar\boldsymbol{\nabla} \to -\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A}. \tag{15.5}$$

Therefore the Schrödinger equation with the Hamiltonian from (15.4) is

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = -\frac{1}{2m}(\hbar\boldsymbol{\nabla} - \mathrm{i}q\boldsymbol{A})^2\Psi + q\Phi\Psi. \tag{15.6}$$

This is the Schrödinger equation for a charged particle in electromagnetic fields. If we write this in the form

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi - q\Phi\Psi = \frac{1}{2m}(\mathrm{i}\hbar\boldsymbol{\nabla} + q\boldsymbol{A})^2\Psi$$

we also recognize a further substitution besides (15.5),

$$\mathrm{i}\hbar\frac{\partial}{\partial t} = \mathrm{i}\hbar c\partial_0 \to \mathrm{i}\hbar c\partial_0 - q\Phi. \tag{15.7}$$

Equations (15.5,15.7) can be combined in 4-vector notation with $p_0 = -E/c$, $A_0 = -\Phi/c$,

$$p_\mu = -\mathrm{i}\hbar\partial_\mu \to p_\mu - qA_\mu = -\mathrm{i}\hbar\partial_\mu - qA_\mu.$$

This observation is useful for recognizing a peculiar symmetry property of equation (15.6). Classical electromagnetism is invariant under gauge transformations of the electromagnetic potentials (here we use $f(x) \equiv f(\boldsymbol{x}, t)$),

$$\Phi(x) \to \Phi'(x) = \Phi(x) - c\partial_0\varphi(x), \quad \boldsymbol{A}(x) \to \boldsymbol{A}'(x) = \boldsymbol{A}(x) + \boldsymbol{\nabla}\varphi(x), \tag{15.8}$$

where the arbitrary function $\varphi(x)$ has the dimension of a magnetic flux, i.e. it comes in units of Vs. The Schrödinger equation (15.6) should respect this invariance of classical electromagnetism to comply with classical limits, and indeed it does. If we also tansform the wave function according to

$$\Psi(x) \to \Psi'(x) = \exp\Big(\mathrm{i}\frac{q}{\hbar}\varphi(x)\Big)\,\Psi(x), \tag{15.9}$$

then the Schrödinger equation in the transformed fields and wave functions has exactly the same form as the Schrödinger equation in the original fields, because the linear transformation property

$$\begin{aligned}
&\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi' - q\Phi'\Psi' + \frac{1}{2m}(\hbar\boldsymbol{\nabla} - \mathrm{i}q\boldsymbol{A}')^2\Psi' \\
&= \exp\Big(\mathrm{i}\frac{q}{\hbar}\varphi(x)\Big)\left[\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi - q\Phi\Psi + \frac{1}{2m}(\hbar\boldsymbol{\nabla} - \mathrm{i}q\boldsymbol{A})^2\Psi\right]
\end{aligned}$$

implies that

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi' - q\Phi'\Psi' + \frac{1}{2m}(\hbar\boldsymbol{\nabla} - \mathrm{i}q\boldsymbol{A}')^2\Psi' = 0$$

holds in the transformed fields if and only if the Schrödinger equation also holds in the original fields,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi - q\Phi\Psi + \frac{1}{2m}(\hbar\boldsymbol{\nabla} - \mathrm{i}q\boldsymbol{A})^2\Psi = 0.$$

The reason for the linear transformation law is

$$\begin{aligned}
\partial_\mu - \mathrm{i}\frac{q}{\hbar}A'_\mu &= \partial_\mu - \mathrm{i}\frac{q}{\hbar}A_\mu - \mathrm{i}\frac{q}{\hbar}(\partial_\mu\varphi) \\
&= \exp\Big(\mathrm{i}\frac{q}{\hbar}\varphi\Big)\Big(\partial_\mu - \mathrm{i}\frac{q}{\hbar}A_\mu\Big)\exp\Big(-\mathrm{i}\frac{q}{\hbar}\varphi\Big),
\end{aligned}$$

which implies that the *covariant derivatives*

$$D_\mu\Psi = \Big(\partial_\mu - \mathrm{i}\frac{q}{\hbar}A_\mu\Big)\,\Psi$$

transform exactly like the fields,

$$\begin{aligned}
&\Psi(x) \to \Psi'(x) = \exp\Big(\mathrm{i}\frac{q}{\hbar}\varphi(x)\Big)\,\Psi(x), \\
&D_\mu\Psi(x) \to D'_\mu\Psi'(x) = \exp\Big(\mathrm{i}\frac{q}{\hbar}\varphi(x)\Big)\,D_\mu\Psi(x),
\end{aligned}$$

$$D_\mu D_\nu \dots D_\rho \Psi(x) \to D'_\mu D'_\nu \dots D'_\rho \Psi'(x) = \exp\left(\mathrm{i}\frac{q}{\hbar}\varphi(x)\right) D_\mu D_\nu \dots D_\rho \Psi(x).$$

This implies preservation of every partial differential equation which like the Schrödinger equation uses only covariant derivatives,

$$\mathrm{i}\hbar c D_0 \Psi(x) = -\frac{\hbar^2}{2m}\boldsymbol{D}^2\Psi(x) \quad \Leftrightarrow \quad \mathrm{i}\hbar c D'_0 \Psi'(x) = -\frac{\hbar^2}{2m}\boldsymbol{D}'^2\Psi'(x).$$

Coupling of matter wave functions to electromagnetic potentials through covariant derivatives is known as *minimal coupling*.

Observables are gauge invariant, too. For example, the mechanical momentum of the charged particle in electromagnetic fields is

$$\begin{aligned} m\frac{d}{dt}\langle \boldsymbol{x}\rangle(t) &= \int d^3\boldsymbol{x}\, \Psi^+(\boldsymbol{x},t)\left[-\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A}(\boldsymbol{x},t)\right]\Psi(\boldsymbol{x},t) \\ &= \int d^3\boldsymbol{x}\, \Psi'^+(\boldsymbol{x},t)\left[-\mathrm{i}\hbar\boldsymbol{\nabla} - q\boldsymbol{A}'(\boldsymbol{x},t)\right]\Psi'(\boldsymbol{x},t). \end{aligned}$$

The mechanical momentum of the particle will generically not be conserved, because it can exchange momentum with the electromagnetic field which carries momentum $\boldsymbol{p}_{em}(t) = \epsilon_0 \int d^3\boldsymbol{x}\, \boldsymbol{E}(\boldsymbol{x},t) \times \boldsymbol{B}(\boldsymbol{x},t)$. The conserved momentum of the system consisting of charged particle and electromagnetic fields is[1] $\boldsymbol{P} = m(d\langle \boldsymbol{x}\rangle(t)/dt) + \boldsymbol{p}_{em}(t)$ (with the mechanical term applying in this form as long as the particle remains non-relativistic, of course).

Electromagnetic interactions ensure local phase invariance of nature. We can rotate the wave function with an arbitrary local phase factor without changing the dynamics or observables of a physical system, due to the presence of the electromagnetic potentials. In hindsight, we should consider this as the reason for the peculiar coupling of the electromagnetic potentials in the Schrödinger equation (15.6).

Multipole moments

In many applications of quantum mechanics, simplifications of the electromagnetic coupling terms in equation (15.6) can be employed if the electromagnetic fields have large wavelengths compared to the wave functions in the Schrödinger equation. The leading order and most common approximation is related to the electric dipole moment of charge distributions, and therefore we will briefly discuss the origin of multipole moments in electromagnetism.

Suppose that we probe the electromagnetic potential of a charge q which is located at $\boldsymbol{x}$. We are interested in the potential at location $\boldsymbol{r}$, where $|\boldsymbol{r}| \gg |\boldsymbol{x}|$. Second order Taylor expansion of the Coulomb term in the variables $\boldsymbol{x}$ yields

$$\frac{q}{|\boldsymbol{r}-\boldsymbol{x}|} \approx \frac{q}{r} + q\frac{\boldsymbol{r}\cdot\boldsymbol{x}}{r^3} + q\frac{3(\boldsymbol{r}\cdot\boldsymbol{x})^2 - r^2\boldsymbol{x}^2}{2r^5} = \frac{q}{r} + \frac{\boldsymbol{r}\cdot\boldsymbol{d}}{r^3} + \frac{1}{2r^5}\boldsymbol{r}\cdot\underline{\mathrm{Q}}\cdot\boldsymbol{r}$$

[1] The canonial momentum $\langle \boldsymbol{p}\rangle(t) = -\mathrm{i}\hbar\int d^3\boldsymbol{x}\, \Psi^+(\boldsymbol{x},t)\boldsymbol{\nabla}\Psi(\boldsymbol{x},t) = m(d\langle \boldsymbol{x}\rangle(t)/dt) + q\langle \boldsymbol{A}(\boldsymbol{x},t)\rangle$ is also generically not conserved, except if the particle moves in a spatially homogeneous electric field $\boldsymbol{E}(t) = -d\boldsymbol{A}(t)/dt$, e.g. in a plate capacitor. However, note that this is an artefact of the gauge $\Phi = 0$.

with the dipole and quadrupole terms

$$\boldsymbol{d} = q\boldsymbol{x}, \quad \underline{\mathrm{Q}} = q\left(3\boldsymbol{x}\otimes\boldsymbol{x} - \boldsymbol{x}^2\underline{1}\right).$$

For an extended charge distribution $\varrho(\boldsymbol{x})$ this implies at large distance a representation of the potential

$$4\pi\epsilon_0\Phi(\boldsymbol{r}) = \int d^3\boldsymbol{x}\,\frac{\varrho(\boldsymbol{x})}{|\boldsymbol{r}-\boldsymbol{x}|} \approx \frac{q}{r} + \frac{\boldsymbol{r}\cdot\boldsymbol{d}}{r^3} + \frac{1}{2r^5}\boldsymbol{r}\cdot\underline{\mathrm{Q}}\cdot\boldsymbol{r}$$

in terms of the the monopole, dipole, and quadrupole moments

$$q = \int d^3\boldsymbol{x}\,\varrho(\boldsymbol{x}), \quad \boldsymbol{d} = \int d^3\boldsymbol{x}\,\varrho(\boldsymbol{x})\boldsymbol{x}, \quad \underline{\mathrm{Q}} = \int d^3\boldsymbol{x}\,\varrho(\boldsymbol{x})[3\boldsymbol{x}\otimes\boldsymbol{x} - \boldsymbol{x}^2\underline{1}].$$

We will find that the leading order coupling of long wavelength electromagnetic fields to charges appears through electric dipole moments of the charges.

Semiclassical treatment of the matter-radiation system in the dipole approximation

In the semiclassical treatment the electromagnetic fields are considered as external classical fields with which the quantum mechanical matter (atom, nucleus, molecule, solid) interacts.
If we consider e.g. an atom with an internal (average or effective) potential $V_{int}(\boldsymbol{x})$ experienced by the electrons, then the Schrödinger equation for these electrons in the external electromagnetic fields is

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi = -\frac{1}{2m}(\hbar\boldsymbol{\nabla} - \mathrm{i}q\boldsymbol{A})^2\psi + (q\Phi + V_{int})\psi. \tag{15.10}$$

If the electromagnetic fields vary weakly over the extension a of the wave functions (corresponding to approximately homogeneous field over the extension of the atom or molecule under consideration), then we can effectively assume a spatially homogeneous field $\boldsymbol{E} = \boldsymbol{E}(t)$ corresponding to a potential $\Phi(\boldsymbol{x}, t) = -\boldsymbol{E}(t)\cdot\boldsymbol{x}$. If we assume that our material probes range over length scales from 1 Å (corresponding to the size of atoms) to several Å (corresponding to molecules containing e.g. several Benzene rings), electromagnetic fields with wavelengths larger than 100 nm or photon energies smaller than 12 eV can be considered as approximately spatially homogeneous over the size of the probe. Furthermore the magnetic field in the electromagnetic wave satisfies

$$\boldsymbol{B}(t) = \frac{1}{2}\boldsymbol{\nabla}\times(\boldsymbol{B}(t)\times\boldsymbol{x})$$

and

$$|\boldsymbol{B}| = \frac{1}{c}|\boldsymbol{E}|, \quad |\dot{\boldsymbol{B}}| = \frac{\omega}{c}|\boldsymbol{E}| = \frac{2\pi}{\lambda}|\boldsymbol{E}|.$$

We have

$$\left|\frac{\partial \boldsymbol{A}}{\partial t}\right| = \frac{1}{2}\left|\dot{\boldsymbol{B}} \times \boldsymbol{x}\right| \simeq \frac{\pi a}{\lambda}\left|\boldsymbol{E}\right| \ll \left|\boldsymbol{E}\right|,$$

and therefore the description of $\boldsymbol{E}$ only through the electric potential,

$$\boldsymbol{E}(t) = -\boldsymbol{\nabla}\Phi(\boldsymbol{x}, t) = \boldsymbol{\nabla}(\boldsymbol{E}(t) \cdot \boldsymbol{x}),$$

is justified for $\lambda \gg a$. Furthermore, the magnitudes of magnetic contributions to the Schrödinger equation are of order

$$\frac{q\hbar}{m}\left|\boldsymbol{A} \cdot \boldsymbol{\nabla}\psi\right| \simeq \frac{q\hbar}{2mc}\left|\boldsymbol{E}\right|\left|\boldsymbol{x}\right|\left|\boldsymbol{\nabla}\psi\right| \simeq \frac{q\hbar}{2mc}\left|\boldsymbol{E}\right|\left|\psi\right|, \tag{15.11}$$

$$\frac{q^2}{2m}\boldsymbol{A}^2\left|\psi\right| \simeq \frac{q^2}{8mc^2}\boldsymbol{E}^2\boldsymbol{x}^2\left|\psi\right| \simeq \frac{q^2a^2}{8mc^2}\boldsymbol{E}^2\left|\psi\right|. \tag{15.12}$$

For comparison, the electric contribution has a magnitude of order

$$q\left|\boldsymbol{E}\right|\left|\boldsymbol{x}\right|\left|\psi\right| \simeq qa\left|\boldsymbol{E}\right|\left|\psi\right|.$$

The ratio of the linear magnetic term (15.11) to the electric term is $\hbar/(2mca)$. If we use the electron mass for m, we find

$$\frac{\hbar}{2mca} \leq 2 \times 10^{-3} \times \frac{1\,\text{Å}}{a},$$

i.e. the linear magnetic term is often negligible compared to the electric term. The ratio of the second magnetic term (15.12) to the electric term is approximately $qa\left|\boldsymbol{E}\right|/8mc^2$. Validity of the non-relativistic approximation requires that the electrostatic energy $qa\left|\boldsymbol{E}\right|$ due to the electric field should be small compared to mc^2. Therefore we also find that the second magnetic term should be negligible compared to the electric term. Quantitatively, if we assume $mc^2 = 511\,\text{keV}$, we have $ea\left|\boldsymbol{E}\right|/8mc^2 \ll 1$ for

$$\left|\boldsymbol{E}\right| \ll \frac{8mc^2}{ea} = 4 \times 10^{16}\frac{\text{V}}{\text{m}} \times \frac{1\,\text{Å}}{a}.$$

For comparison, the internal field strength in hydrogen is of order $e/(4\pi\epsilon_0 a_0^2)$ $\simeq 5 \times 10^{11}\,\text{V/m}$.
We conclude that for $\lambda \gg a$ the effect of external electromagnetic fields can be approximated by the addition of a term

$$\Delta V(\mathbf{x}, t) = q\Phi(\mathbf{x}, t) = -q\boldsymbol{E}(t) \cdot \mathbf{x} = -\boldsymbol{d} \cdot \boldsymbol{E}(t) \tag{15.13}$$

in the Schrödinger equation. The approximation of spatially homogeneous external field yields a perturbation proportional to the dipole operator and is therefore denoted as *dipole approximation*.

Two cautionary remarks are in order at this point. The term *dipole approximation* is nowadays more widely used for the long wavelength approximation $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \simeq 1$ in matrix elements irrespective of whether the perturbation operator has the dipole form (15.13) or is given in terms of the coupling to the vector potential $\boldsymbol{A}(\mathbf{x}, t)$ in (15.10).
Furthermore, if we describe electromagnetic interactions at the level of photon-matter interactions, the dipole approximation (15.13) is generally limited to first order perturbation theory, and holds in second order perturbation theory only if additional conditions are met, see Section 18.8 and Problem 18.3.

Dipole selection rules

The first order scattering matrix elements in dipole approximation are given by $S_{fi} = \sqrt{2\pi}\mathrm{i}q\boldsymbol{E}(\omega_{fi})\cdot\langle f|\mathbf{x}|i\rangle/\hbar$, i.e. only transitions $|i\rangle \to |f\rangle$ with non-vanishing dipole matrix elements $q\langle f|\mathbf{x}|i\rangle$ are allowed in this approximation. This yields straigthforward selection rules for states which are eigenstates of $\boldsymbol{M}^2$ and M_z. The commutator relation $[M_z, \mathrm{z}] = 0$ implies

$$\langle n', \ell', m'|[M_z, \mathrm{z}]|n, \ell, m\rangle = \hbar\langle n', \ell', m'|\mathrm{z}|n, \ell, m\rangle(m' - m) = 0, \tag{15.14}$$

and therefore an electric field component in z direction can only induce transitions between states with the same magnetic quantum number.
In the same way, the commutators $[M_z, \mathrm{x} \pm \mathrm{iy}] = \pm\hbar(\mathrm{x} \pm \mathrm{iy})$ imply

$$\langle n', \ell', m'|\mathrm{x} \pm \mathrm{iy}|n, \ell, m\rangle(m' - m \mp 1) = 0, \tag{15.15}$$

such that electric field components in the (x, y) plane can only induce transitions which increase or decrease the magnetic quantum number by one unit.
Finally, the fairly complicated relation $[\boldsymbol{M}^2, [\boldsymbol{M}^2, \mathbf{x}]] = 2\hbar^2\{\boldsymbol{M}^2, \mathbf{x}\}$ yields

$$\langle n', \ell', m'|\mathbf{x}|n, \ell, m\rangle(\ell + \ell')(\ell + \ell' + 2)[(\ell - \ell')^2 - 1] = 0. \tag{15.16}$$

This implies that the matrix element can be non-vanishing only if $\ell' = \ell \pm 1$. $\ell' = \ell = 0$ is not a solution, because in this case the wave functions depend only on r and the angular integrations show that the matrix element vanishes in this case.
Equations (15.14-15.16) imply the dipole selection rules $\Delta\ell = \pm 1$ and $\Delta m = 0, \pm 1$.

15.2 Stark effect and static polarizability tensors

Polarizability tensors characterize the response of a quantum system to an external electric field $\boldsymbol{E}$. The calculation of polarizability tensors is another

example of applications of second order perturbation theory in materials science. It also illustrates the role of perturbation theory in derivations of quantum mechanical expressions for measurable physical quantities, which were first introduced in classical electrodynamics and were initially approximated by means of simple mechanical models.

The calculation of polarizabilities generically involves many particles and related dipole operators $V(t) = -\sum_{i=1}^{N} q_i \boldsymbol{E}(t) \cdot \mathbf{x}_i$, where it is assumed that all particles are confined to a region which is still small compared to the wavelength of the electric field. We will develop the theory in a single-particle approximation in the sense that we only use the single charged (quasi-)particle operator $V(t) = -q\boldsymbol{E}(t) \cdot \mathbf{x}$. In the present section we will do this for time-independent external field, where we can use the techniques of time-independent perturbation theory. The case of dynamical polarizability for time-dependent external fields will be discussed in Section 15.3.

Linear Stark effect

Before we jump into the second order calculation of the response to an electric field, we consider the implications of first order perturbation theory for the dipole approximation.

An external static electric field shifts the Hamilton operator according to

$$H_0 \to H = H_0 + V = H_0 - q\boldsymbol{E} \cdot \mathbf{x}.$$

Time-independent perturbation theory tells us that the first order shifts of atomic or molecular energy levels due to the external field have to be determined as the eigenvalues of the matrix

$$\langle \psi_{n,\alpha}^{(0)} | V(\mathbf{x}) | \psi_{n,\beta}^{(0)} \rangle = -q \langle \psi_{n,\alpha}^{(0)} | \mathbf{x} | \psi_{n,\beta}^{(0)} \rangle \cdot \boldsymbol{E},$$

and when the n-th degeneracy subspace has been internally diagonalized with respect to $V(\mathbf{x})$, the first order shifts are

$$E_{n,\alpha}^{(1)} = -q \langle \psi_{n,\alpha}^{(0)} | \mathbf{x} | \psi_{n,\alpha}^{(0)} \rangle \cdot \boldsymbol{E} = -\boldsymbol{d}_{n,\alpha} \cdot \boldsymbol{E},$$

with the *intrinsic* dipole moment in the state $|\psi_{n,\alpha}^{(0)}\rangle$

$$\boldsymbol{d}_{n,\alpha} = q \langle \psi_{n,\alpha}^{(0)} | \mathbf{x} | \psi_{n,\alpha}^{(0)} \rangle. \tag{15.17}$$

The perturbation V has odd parity under $\boldsymbol{x} \to -\boldsymbol{x}$, while atomic states of opposite parity are usually not degenerate. Therefore in systems which are symmetric under the parity transformation $\boldsymbol{x} \to -\boldsymbol{x}$, the states in the n-th energy level usually satisfy

$$\langle \psi_{n,\alpha}^{(0)} | \mathbf{x} | \psi_{n,\beta}^{(0)} \rangle = 0$$

because the integrand is odd under the parity transformation. Usually this implies absence of a linear Stark effect in atoms, and the same remark applies

to molecules with parity symmetry. An important exception is the hydrogen atom due to ℓ-degeneracy of its energy levels (if the matrix elements of V are larger than the fine structure of the hydrogen levels). States with angular momentum quantum number ℓ have parity $(-1)^\ell$, so that the n-th hydrogen level with $n > 1$ contains degenerate states of opposite parity. Diagnalization of V in that degeneracy subspace then yields states $|\psi^{(0)}_{n,\alpha}\rangle$ with $\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \neq 0$.

Quadratic Stark effect and the static polarizability tensor

Second order perturbation theory yields the following corrections to discrete atomic or molecular energy levels,

$$E^{(2)}_{n\alpha} = \sum\!\!\!\!\!\!\int_{m\neq n} \sum_\beta \frac{|\langle\psi^{(0)}_{m\beta}|V|\psi^{(0)}_{n\alpha}\rangle|^2}{E^{(0)}_n - E^{(0)}_m}$$
$$= q^2 \boldsymbol{E}\cdot \sum\!\!\!\!\!\!\int_{m\neq n} \sum_\beta \frac{\langle\psi^{(0)}_{n\alpha}|\mathbf{x}|\psi^{(0)}_{m\beta}\rangle\langle\psi^{(0)}_{m\beta}|\mathbf{x}|\psi^{(0)}_{n\alpha}\rangle}{E^{(0)}_n - E^{(0)}_m}\cdot \boldsymbol{E}.$$

The notation takes into account that the intermediate levels can be continuous, but degeneracy indices are always discrete.
We can write the second order shifts in the form

$$E^{(2)}_{n\alpha} = -\frac{1}{2}\,\boldsymbol{d}_{(n\alpha)}\cdot\boldsymbol{E} = -\frac{1}{2}\,\boldsymbol{E}\cdot\underline{\alpha}_{(n\alpha)}\cdot\boldsymbol{E},$$

where

$$\boldsymbol{d}_{(n\alpha)} = \underline{\alpha}_{(n\alpha)}\cdot\boldsymbol{E}$$

is the *induced* dipole moment and $\underline{\alpha}_{(n\alpha)}$ is the static electronic polarizability tensor in the state $|\psi^{(0)}_{n\alpha}\rangle$,

$$\underline{\alpha}_{(n\alpha)} = -q^2 \sum\!\!\!\!\!\!\int_{m\neq n} \sum_\beta \frac{1}{E^{(0)}_n - E^{(0)}_m}\Big(\langle\psi^{(0)}_{n\alpha}|\mathbf{x}|\psi^{(0)}_{m\beta}\rangle\otimes\langle\psi^{(0)}_{m\beta}|\mathbf{x}|\psi^{(0)}_{n\alpha}\rangle$$
$$+\langle\psi^{(0)}_{m\beta}|\mathbf{x}|\psi^{(0)}_{n\alpha}\rangle\otimes\langle\psi^{(0)}_{n\alpha}|\mathbf{x}|\psi^{(0)}_{m\beta}\rangle\Big). \tag{15.18}$$

Note that in the ground state $\alpha_{ii} > 0$ (no summation convention), i.e. in second order perturbation theory, which usually should capture all linear contributions from a weak external electric field to the induced dipole moment, there is no electronic dia-electricity for the ground state.

15.3 Dynamical polarizability tensors

We cannot use time-independent perturbation theory if the perturbation operator $V(t) = -q\mathbf{x}\cdot\boldsymbol{E}(t)$ varies with time. Application of our results from

Chapter 13 for time-dependent perturbations implies that the first order transition probability from a state $|m\rangle$ into a state $|n\rangle$ under the action of the electric field $\boldsymbol{E}(t)$ between times t' and t is proportional to[2]

$$P^{(1)}_{m\to n}(t,t') = \left| \frac{q}{\hbar} \int_{t'}^{t} d\tau \, \exp(\mathrm{i}\omega_{nm}\tau) \boldsymbol{E}(\tau) \cdot \langle n|\mathbf{x}|m\rangle \right|^2 ,$$

where

$$\omega_{nm} = \frac{1}{\hbar}(E_n - E_m).$$

For $t' \to -\infty$, $t \to \infty$, this becomes in particular (see our previous results (13.21,13.22))

$$P^{(1)}_{m\to n} = 2\pi \left| \frac{q}{\hbar} \boldsymbol{E}(\omega_{nm}) \cdot \langle n|\mathbf{x}|m\rangle \right|^2 ,$$

i.e. long term action of an external electric field can induce a transition in first order between energy levels E_m and E_n only if the field contains a Fourier component of the corresponding frequency ω_{nm}.
However, at this time we are interested in the problem how equation (15.18) can be generalized to a dynamical polarizability in the presence of a time-dependent external field $\boldsymbol{E}(t)$.
Suppose the system was in the state $|\psi^{(0)}_{n,\alpha}(0)\rangle \equiv |\psi^{(0)}_{n,\alpha}\rangle$ at $t = 0$, when it begins to experience the effect of the electric field. The shift of the wave function $|\psi^{(0)}_{n,\alpha}(t)\rangle$ under the influence of the external field is

$$\begin{aligned} |\psi_{n,\alpha}(t)\rangle - |\psi^{(0)}_{n,\alpha}(t)\rangle &= \Theta(t)\left[U(t) - U_0(t)\right] |\psi^{(0)}_{n,\alpha}\rangle \\ &= \Theta(t)U_0(t)\left[U_0^+(t)U(t)U_0(0) - 1\right] |\psi^{(0)}_{n,\alpha}\rangle \\ &= \Theta(t)U_0(t)\left[U_D(t) - 1\right] |\psi^{(0)}_{n,\alpha}\rangle, \end{aligned}$$

and the first order shift is therefore

$$\begin{aligned} |\psi^{(1)}_{n,\alpha}(t)\rangle &= -\frac{\mathrm{i}}{\hbar}\Theta(t)U_0(t) \int_0^t d\tau \, H_D(\tau) |\psi^{(0)}_{n,\alpha}\rangle \\ &= -\frac{\mathrm{i}}{\hbar}\Theta(t)U_0(t) \int_0^t d\tau \, U_0^+(\tau)V(\tau)U_0(\tau) |\psi^{(0)}_{n,\alpha}\rangle \\ &= -\frac{\mathrm{i}}{\hbar}\Theta(t) \int_0^t d\tau \, U_0(t-\tau)V(\tau)U_0(\tau) |\psi^{(0)}_{n,\alpha}\rangle. \end{aligned}$$

The *induced* dipole moment in the state $|\psi^{(0)}_{n,\alpha}\rangle$ is then given in leading order by the first order terms (recall that the 0th order term corresponds to the

[2]Recall that $|S_{nm}|^2$ is a true transition probability only if the initial and final state are discrete, while otherwise it enters into decay rates or cross sections.

intrinsic dipole moment (15.17))

$$\begin{aligned}\boldsymbol{d}_{(n\alpha)}(t) &= \langle\psi^{(0)}_{n,\alpha}(t)|q\mathbf{x}|\psi^{(1)}_{n,\alpha}(t)\rangle + \langle\psi^{(1)}_{n,\alpha}(t)|q\mathbf{x}|\psi^{(0)}_{n,\alpha}(t)\rangle \\ &= q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\int_0^t d\tau\,\langle\psi^{(0)}_{n,\alpha}|U_0^+(t)\mathbf{x}U_0(t-\tau)\mathbf{x}\cdot\boldsymbol{E}(\tau)U_0(\tau)|\psi^{(0)}_{n,\alpha}\rangle \\ &\quad -q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\int_0^t d\tau\,\langle\psi^{(0)}_{n,\alpha}|U_0^+(\tau)\mathbf{x}\cdot\boldsymbol{E}(\tau)U_0^+(t-\tau)\mathbf{x}U_0(t)|\psi^{(0)}_{n,\alpha}\rangle.\end{aligned}$$

This becomes after insertion of complete sets of unperturbed states in $U_0(t-\tau) = U_0(t)U_0^+(\tau)$ and $U_0^+(t-\tau) = U_0(\tau)U_0^+(t)$

$$\begin{aligned}\boldsymbol{d}_{(n\alpha)}(t) &= q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\sum\!\!\!\!\!\!\int_{m,\beta}\int_0^t d\tau\,\exp[\mathrm{i}\omega_{nm}(t-\tau)]\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle \\ &\quad\times\langle\psi^{(0)}_{m,\beta}|\mathbf{x}\cdot\boldsymbol{E}(\tau)|\psi^{(0)}_{n,\alpha}\rangle - q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\sum\!\!\!\!\!\!\int_{m,\beta}\int_0^t d\tau\,\exp[-\mathrm{i}\omega_{nm}(t-\tau)] \\ &\quad\times\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}\cdot\boldsymbol{E}(\tau)|\psi^{(0)}_{m,\beta}\rangle\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \\ &= \int_0^\infty d\tau\,\underline{\alpha}_{(n\alpha)}(t-\tau)\cdot\boldsymbol{E}(\tau),\end{aligned} \tag{15.19}$$

with a dynamical polarizability tensor

$$\begin{aligned}\underline{\alpha}_{(n\alpha)}(t) &= q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\sum\!\!\!\!\!\!\int_{m,\beta}\exp(\mathrm{i}\omega_{nm}t)\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle\otimes\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \\ &\quad -q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\sum\!\!\!\!\!\!\int_{m,\beta}\exp(-\mathrm{i}\omega_{nm}t)\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle\otimes\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle.\end{aligned} \tag{15.20}$$

Now we assume harmonic time dependence of an electric field which is switched on at $t = 0$,

$$\boldsymbol{E}(\tau) \equiv \boldsymbol{E}_\omega(\tau) = \boldsymbol{E}\Theta(t)\sin(\omega\tau) = \boldsymbol{E}\Theta(t)\,\frac{\exp(\mathrm{i}\omega\tau) - \exp(-\mathrm{i}\omega\tau)}{2\mathrm{i}}.$$

The time integrals in the two terms for $\boldsymbol{d}_{(n\alpha)}(t)$ then yield

$$\begin{aligned}&\pm\frac{q^2}{2\hbar}\int_0^t d\tau\Big(\exp[\pm\mathrm{i}\omega_{nm}(t-\tau)+\mathrm{i}\omega\tau] - \exp[\pm\mathrm{i}\omega_{nm}(t-\tau)-\mathrm{i}\omega\tau]\Big) \\ &= \pm\frac{q^2}{2\mathrm{i}\hbar}\left(\frac{\exp(\mathrm{i}\omega t) - \exp(\pm\mathrm{i}\omega_{nm}t)}{\omega\mp\omega_{nm}} + \frac{\exp(-\mathrm{i}\omega t) - \exp(\pm\mathrm{i}\omega_{nm}t)}{\omega\pm\omega_{nm}}\right) \\ &= \pm\frac{q^2}{\mathrm{i}\hbar}\frac{\omega\cos(\omega t)\pm\mathrm{i}\omega_{nm}\sin(\omega t) - \omega\exp(\pm\mathrm{i}\omega_{nm}t)}{\omega^2-\omega_{nm}^2}.\end{aligned} \tag{15.21}$$

We also assume slowly oscillating field in the sense $\omega \ll |\omega_{nm}|$ for all quantum numbers m which correspond to large matrix elements $|\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle|$. This means that the external field is not likely to induce direct transitions between

different energy levels. Under these conditions, the contribution from the integrals in equation (15.21) to $\boldsymbol{d}_{(n\alpha)}(t)$ will be dominated by the term which is in phase with the external field,

$$\pm\frac{q^2}{2\hbar}\int_0^t d\tau\Big(\exp[\pm\mathrm{i}\omega_{nm}(t-\tau)+\mathrm{i}\omega\tau]-\exp[\pm\mathrm{i}\omega_{nm}(t-\tau)-\mathrm{i}\omega\tau]\Big)$$

$$\to\frac{q^2}{\hbar}\frac{\omega_{nm}\sin(\omega t)}{\omega^2-\omega_{nm}^2},$$

and the induced dipole moment in this approximation is

$$\begin{aligned}\boldsymbol{d}_{(n\alpha)\omega}(t)=\frac{q^2}{\hbar}\sum\!\!\!\!\!\!\int_{m,\beta}\frac{\omega_{mn}}{\omega_{mn}^2-\omega^2}\Big(&\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle\langle\psi^{(0)}_{m,\beta}|\mathbf{x}\cdot\boldsymbol{E}_\omega(t)|\psi^{(0)}_{n,\alpha}\rangle\\&+\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}\cdot\boldsymbol{E}_\omega(t)|\psi^{(0)}_{m,\beta}\rangle\Big).\end{aligned}$$

This can also be written as

$$\boldsymbol{d}_{(n\alpha)\omega}(t)=\underline{\alpha}_{(n\alpha)}(\omega)\cdot\boldsymbol{E}_\omega(t)$$

with the frequency dependent polarizability tensor for the state $|\psi^{(0)}_{n,\alpha}\rangle$ (usually the ground state)

$$\begin{aligned}\underline{\alpha}_{(n\alpha)}(\omega)=\frac{q^2}{\hbar}\sum\!\!\!\!\!\!\int_{m,\beta}\frac{\omega_{mn}}{\omega_{mn}^2-\omega^2}\Big(&\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle\otimes\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle\\&+\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle\otimes\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle\Big).\end{aligned}\tag{15.22}$$

The zero frequency polarizability tensor $\underline{\alpha}_{(n\alpha)}(0)$ is the static tensor (15.18), as expected.
The frequency dependent polarizability tensor is not only relevant for slowly oscillating fields, but appears implicitly already in the equations (15.19,15.20), which do not include a restriction to slowly oscillating external field. If we agree to shift the denominator in (15.22) by small imaginary numbers according to

$$\begin{aligned}\underline{\alpha}_{(n\alpha)}(\omega)=&\frac{q^2}{\hbar}\sum\!\!\!\!\!\!\int_{m,\beta}\frac{\omega_{nm}}{\omega^2-\omega_{nm}^2-\mathrm{i}\epsilon}\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle\otimes\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle\\&+\frac{q^2}{\hbar}\sum\!\!\!\!\!\!\int_{m,\beta}\frac{\omega_{nm}}{\omega^2-\omega_{nm}^2+\mathrm{i}\epsilon}\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle\otimes\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle,\end{aligned}$$

we find that the dynamical polarizability tensors in equations (15.20) and (15.22) are related via

$$\underline{\alpha}_{(n\alpha)}(t)=\frac{\Theta(t)}{\pi}\int_{-\infty}^{\infty}d\omega\,\underline{\alpha}_{(n\alpha)}(\omega)\exp(-\mathrm{i}\omega t).\tag{15.23}$$

Oscillator strength

Equation (15.22) yields an averaged polarizability

$$\alpha_{(n\alpha)}(\omega) = \frac{1}{3}\mathrm{tr}\,\underline{\alpha}_{(n\alpha)}(\omega) = \frac{2q^2}{3\hbar}\sum\!\!\!\!\!\!\int_{m,\beta} \frac{\omega_{mn}}{\omega_{mn}^2-\omega^2}|\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle|^2$$
$$= \frac{q^2}{m}\sum\!\!\!\!\!\!\int_{m,\beta} \frac{f_{m,\beta;n,\alpha}}{\omega_{mn}^2-\omega^2}$$

with the *oscillator strength* for the transition $|\psi^{(0)}_{n,\alpha}\rangle \to |\psi^{(0)}_{m,\beta}\rangle$:

$$f_{m,\beta;n,\alpha} = \frac{2m}{3\hbar}\omega_{mn}|\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle|^2 = -f_{n,\alpha;m,\beta}. \tag{15.24}$$

We use m both for the mass of the charged (quasi-)particle which has its wave functions shifted due to the external field, and as a label for the intermediate states. Since mass never appears as an index in equation (15.24) or the following equations, this should not cause confusion.

The polarizability is also often averaged over degenerate initial states. If the degeneracy of the n-th energy level is g_n, then

$$\alpha_n(\omega) = \frac{1}{g_n}\sum_{\alpha}\alpha_{(n\alpha)}(\omega) = \frac{q^2}{m}\sum\!\!\!\!\!\!\int_{m} \frac{f_{m|n}}{\omega_{mn}^2-\omega^2}$$

with an effective oscillator strength which is averaged over degenerate initial states and summed over degenerate final states,

$$f_{m|n} = \frac{1}{g_n}\sum_{\alpha,\beta} f_{m,\beta;n,\alpha} = -\frac{g_m}{g_n}f_{n|m}. \tag{15.25}$$

With these conventions, positive oscillator strength corresponds to absorption and negative oscillator strength corresponds to emission. Oscillator strengths are sometimes also defined through absolute values, but for the f-sum rules below it plays a role that emission transitions contribute with negative sign.

For an explanation of the name *oscillator strength* for $f_{m,\beta;n,\alpha}$, we observe that a classical isotropic harmonic oscillator model for polarizability

$$m\ddot{\boldsymbol{x}}(t) + m\omega_0^2\boldsymbol{x}(t) = q\boldsymbol{E}\sin(\omega t)$$

yields an induced dipole moment

$$\boldsymbol{d}_\omega(t) = q\boldsymbol{x}(t) = \frac{q^2}{m}\frac{1}{\omega_0^2-\omega^2}\boldsymbol{E}\sin(\omega t) = \alpha(\omega)\boldsymbol{E}_\omega(t)$$

with the polarizability

$$\alpha(\omega) = \frac{q^2}{m}\frac{1}{\omega_0^2-\omega^2},$$

i.e. every virtual transition $|\psi^{(0)}_{n,\alpha}\rangle \to |\psi^{(0)}_{m,\beta}\rangle$ contributes effectively like an oscillator of frequency $|\omega_{mn}| = \left|E^{(0)}_m - E^{(0)}_n\right|/\hbar$ to the polarizability $\alpha_{(n\alpha)}(\omega)$ of the state $|\psi^{(0)}_{n,\alpha}\rangle$, but the contribution of that transition is weighted with the oscillator strength (15.24).

Thomas-Reiche-Kuhn sum rule (f-sum rule) for the oscillator strength

Kuhn, Reiche and Thomas found a sum rule for the oscillator strength already in the framework of old quantum theory[3]. The quantum mechanical proof is based on the fact that the Hamiltonian operator $H = (\mathbf{p}^2/2m) + V(\mathbf{x})$ yields a commutator

$$[H, \mathbf{x}] = \frac{\hbar \mathbf{p}}{\mathrm{i}m}. \tag{15.26}$$

This implies for a discrete normalized state $|\psi^{(0)}_{n,\alpha}\rangle$

$$\begin{aligned}
\sum\!\!\!\!\!\!\int_{m,\beta} f_{m,\beta;n,\alpha} &= \frac{2m}{3\hbar} \sum\!\!\!\!\!\!\int_{m,\beta} \omega_{mn} \langle \psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle \cdot \langle \psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \\
&= \frac{2m}{3\hbar^2} \sum\!\!\!\!\!\!\int_{m,\beta} \left(E^{(0)}_m - E^{(0)}_n\right) \langle \psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle \cdot \langle \psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \\
&= \frac{m}{3\hbar^2} \sum\!\!\!\!\!\!\int_{m,\beta} \Big(\langle \psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle \cdot \langle \psi^{(0)}_{m,\beta}|[H_0, \mathbf{x}]|\psi^{(0)}_{n,\alpha}\rangle \\
&\quad - \langle \psi^{(0)}_{n,\alpha}|[H_0, \mathbf{x}]|\psi^{(0)}_{m,\beta}\rangle \cdot \langle \psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \Big) \\
&= \frac{1}{3\mathrm{i}\hbar} \sum\!\!\!\!\!\!\int_{m,\beta} \Big(\langle \psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle \cdot \langle \psi^{(0)}_{m,\beta}|\mathbf{p}|\psi^{(0)}_{n,\alpha}\rangle \\
&\quad - \langle \psi^{(0)}_{n,\alpha}|\mathbf{p}|\psi^{(0)}_{m,\beta}\rangle \cdot \langle \psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \Big) \\
&= \frac{1}{3\mathrm{i}\hbar} \langle \psi^{(0)}_{n,\alpha}|[\mathbf{x}\ ;\ \mathbf{p}]|\psi^{(0)}_{n,\alpha}\rangle = 1.
\end{aligned}$$

This is the[4] *Thomas-Reiche-Kuhn sum rule*,

$$\sum\!\!\!\!\!\!\int_{m,\beta} f_{m,\beta;n,\alpha} = 1. \tag{15.27}$$

Averaging over initial degeneracy indices (15.25) then also yields

$$\sum\!\!\!\!\!\!\int_{m} f_{m|n} = 1. \tag{15.28}$$

Equation (15.26) implies a further relation which connects matrix elements of $\mathbf{x}$ and $\mathbf{p}$,

$$\omega_{mn} \langle \psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle = \frac{1}{\mathrm{i}m} \langle \psi^{(0)}_{m,\beta}|\mathbf{p}|\psi^{(0)}_{n,\alpha}\rangle.$$

This yields an alternative representation of the oscillator strength

$$f_{m,\beta;n,\alpha} = \frac{2}{3m\hbar\omega_{mn}} |\langle \psi^{(0)}_{m,\beta}|\mathbf{p}|\psi^{(0)}_{n,\alpha}\rangle|^2, \tag{15.29}$$

[3] W. Kuhn, Z. Phys. 33, 408 (1925); F. Reiche & W. Thomas, Z. Phys. 34, 510 (1925).

[4] If the wave functions are N-particle wave functions and V is the corresponding sum of dipole operators, the number on the right hand side of the sum rules becomes N.

which is known as the *velocity form* of the oscillator strength, while equation (15.24) is denoted as the *length form* of the oscillator strength. Yet another common definition in atomic, molecular and optical physics is

$$f_{m,\beta;n,\alpha} = \frac{2m\omega_{mn}}{3\hbar q^2}\mathcal{S}_{m,\beta;n,\alpha}, \quad f_{m|n} = \frac{2m\omega_{mn}}{3\hbar q^2}\mathcal{S}_{m,n},$$

with the *electric dipole line strength* of the transition $|\psi^{(0)}_{n,\alpha}\rangle \to |\psi^{(0)}_{m,\beta}\rangle$

$$\mathcal{S}_{m,\beta;n,\alpha} = |\langle\psi^{(0)}_{m,\beta}|q\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle|^2 = \left|\frac{q}{m\omega_{mn}}\langle\psi^{(0)}_{m,\beta}|\mathbf{p}|\psi^{(0)}_{n,\alpha}\rangle\right|^2,$$

$$\mathcal{S}_{m,n} = \frac{1}{g_n}\sum_{\alpha,\beta}\mathcal{S}_{m,\beta;n,\alpha} = \frac{g_m}{g_n}\mathcal{S}_{n,m}.$$

Tensorial oscillator strengths and sum rules

We can define oscillator strength tensors through the relations

$$\underline{\alpha}_{(n\alpha)}(\omega) = \frac{q^2}{m}\sum\!\!\!\!\!\!\int_{m,\beta}\frac{\underline{f}_{m,\beta;n,\alpha}}{\omega^2_{mn}-\omega^2},$$

$$\underline{\alpha}_{n}(\omega) = \frac{1}{g_n}\sum_{\alpha}\underline{\alpha}_{(n\alpha)}(\omega) = \frac{q^2}{m}\sum_{m}\frac{\underline{f}_{m,n}}{\omega^2_{mn}-\omega^2},$$

i.e. we have representations for oscillator strength tensors

$$\begin{aligned}
\underline{f}_{m,\beta;n,\alpha} &= \frac{m}{\hbar}\omega_{mn}\Big(\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle\otimes\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \\
&\quad +\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle\otimes\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle\Big) \\
&= \frac{m}{2\hbar^2}\Big(\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle\otimes\langle\psi^{(0)}_{m,\beta}|[H_0,\mathbf{x}]|\psi^{(0)}_{n,\alpha}\rangle \\
&\quad -\langle\psi^{(0)}_{n,\alpha}|[H_0,\mathbf{x}]|\psi^{(0)}_{m,\beta}\rangle\otimes\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \\
&\quad +\langle\psi^{(0)}_{m,\beta}|[H_0,\mathbf{x}]|\psi^{(0)}_{n,\alpha}\rangle\otimes\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle \\
&\quad -\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle\otimes\langle\psi^{(0)}_{n,\alpha}|[H_0,\mathbf{x}]|\psi^{(0)}_{m,\beta}\rangle\Big) \\
&= \frac{1}{2\mathrm{i}\hbar}\Big(\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle\otimes\langle\psi^{(0)}_{m,\beta}|\mathbf{p}|\psi^{(0)}_{n,\alpha}\rangle \\
&\quad -\langle\psi^{(0)}_{n,\alpha}|\mathbf{p}|\psi^{(0)}_{m,\beta}\rangle\otimes\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle \\
&\quad +\langle\psi^{(0)}_{m,\beta}|\mathbf{p}|\psi^{(0)}_{n,\alpha}\rangle\otimes\langle\psi^{(0)}_{n,\alpha}|\mathbf{x}|\psi^{(0)}_{m,\beta}\rangle \\
&\quad -\langle\psi^{(0)}_{m,\beta}|\mathbf{x}|\psi^{(0)}_{n,\alpha}\rangle\otimes\langle\psi^{(0)}_{n,\alpha}|\mathbf{p}|\psi^{(0)}_{m,\beta}\rangle\Big) \\
&= -\underline{f}_{n,\alpha;m,\beta},
\end{aligned} \tag{15.30}$$

and reduced oscillator strength tensors

$$\underline{f}_{m|n} = \frac{1}{g_n}\sum_{\alpha,\beta}\underline{f}_{m,\beta;n,\alpha} = -\frac{g_m}{g_n}\underline{f}_{n|m}. \tag{15.31}$$

This yields tensorial f-sum rules,

$$\sum_{m,\beta} \underline{f}_{m,\beta;n,\alpha} = \frac{1}{2\mathrm{i}\hbar} \langle \psi^{(0)}_{n,\alpha}| \left([\mathrm{x}_i, \mathrm{p}_j] - [\mathrm{p}_i, \mathrm{x}_j]\right) |\psi^{(0)}_{n,\alpha}\rangle \boldsymbol{e}_i \otimes \boldsymbol{e}_j = \underline{1} = \sum_m \underline{f}_{m|n}.$$

For comparison, we note that the polarization tensor of an isotropic classical oscillator is easily shown to be

$$\underline{\alpha}(\omega) = \frac{q^2}{m} \frac{1}{\omega_0^2 - \omega^2} \underline{1}.$$

The standard oscillator strength is related to the oscillator strength tensor via

$$f_{m,\beta;n,\alpha} = \frac{1}{3} \mathrm{tr}\, \underline{f}_{m,\beta;n,\alpha}.$$

15.4 Problems

15.1 Show that the probability current density in the presence of electromagnetic potentials is given by

$$\boldsymbol{j} = \frac{\hbar}{2\mathrm{i}m} \left(\psi^+ \boldsymbol{\nabla} \psi - \boldsymbol{\nabla} \psi^+ \cdot \psi - 2\mathrm{i} \frac{q}{\hbar} \psi^+ \boldsymbol{A} \psi \right).$$

Is this expression gauge invariant?

15.2 A hydrogen atom is initially in its ground state when it is excited by an external electric field $\boldsymbol{E}(t)$.
2a. Show through direct evaluation of the matrix elements that the dipole term $V(t) = -q\mathbf{x} \cdot \boldsymbol{E}(t)$ in first order only excites higher level p states.
2b. The external field is

$$\boldsymbol{E}(t) = \boldsymbol{e}_z \mathcal{E} \exp(-t^2/\tau^2). \tag{15.32}$$

How large are the first order transition probabilities $P_{1\to n}$ into excited bound energy levels?

15.3 How large is the ionization probability for a hydrogen atom in the electric field (15.32) in leading order perturbation theory?

15.4 Calculate the linear Stark effect for the first excited level of hydrogen due to a homogeneous static electric field $\boldsymbol{E}$.

15.5 Calculate the static polarizability tensor in the ground state of hydrogen.

15.6 Calculate the oscillator strengths $f_{n';n} = 2m\omega_{n'n} |\langle n'|x|n\rangle|^2/\hbar$ for a one-dimensional oscillator. Why does the equation for the one-dimensional oscillator strength differ by a factor 3 from the three-dimensional oscillator strength (15.24)?

15.7 Calculate the oscillator strengths $f_{n,\ell,m;1,0,0}$ for the hydrogen atom. How large is the sum

$$\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \int_0^{\infty} dk\, k^2 f_{k,\ell,m;1,0,0}$$

of the oscillator strengths into Coulomb waves?

15.8 We consider the transition $|m\rangle \to |n\rangle$ due to an external electric field $\boldsymbol{E}(t)$. Show that the square of the corresponding first order scattering matrix element is related to the oscillator strength tensor of the transition through

$$|S_{nm}|^2 = \frac{\pi q^2}{m\hbar\omega_{nm}} \boldsymbol{E}(\omega_{nm}) \cdot \underline{f}_{n;m} \cdot \boldsymbol{E}(\omega_{nm}).$$

15.9 Show that normalizable energy eigenstates, $\langle n|n\rangle = 1$, have vanishing momentum expectation values,

$$\langle n|\mathbf{p}|n\rangle = 0.$$

Why does this equation not hold for plane wave states?

15.10 Prove the *Bethe sum rule*[5],

$$\frac{2m}{\hbar} \sum\!\!\!\!\!\!\int_{m,\beta} \omega_{mn} \left| \langle \psi^{(0)}_{m,\beta}| \exp(\mathrm{i}\boldsymbol{k}\cdot\mathbf{x}) |\psi^{(0)}_{n,\alpha}\rangle \right|^2 = \boldsymbol{k}^2.$$

[5] H. Bethe, Annalen Phys. 397, 325 (1930).

Chapter 16

Principles of Lagrangian Field Theory

The replacement of Newton's equation by quantum mechanical wave equations in the 1920s implied that by that time all known fundamental degrees of freedom in physics were described by fields like $\boldsymbol{A}(\boldsymbol{x},t)$ or $\Psi(\boldsymbol{x},t)$, and their dynamics was encoded in wave equations. However, all the known fundamental wave equations can be derived from a field theory version of Hamilton's principle[1], i.e. the concept of the Lagrange function $L(q(t),\dot{q}(t))$ and the related action $S=\int dt\, L$ generalizes to a Lagrange density $\mathcal{L}(\phi(\boldsymbol{x},t),\dot{\phi}(\boldsymbol{x},t),\boldsymbol{\nabla}\phi(\boldsymbol{x},t))$ with related action $S=\int dt\int d^3\boldsymbol{x}\,\mathcal{L}$, such that all fundamental wave equations can be derived from the variation of an action,

$$\frac{\partial\mathcal{L}}{\partial\phi}-\partial_\mu\frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi)}=0.$$

This formulation of dynamics is particularly useful for exploring the connection between symmetries and conservation laws of physical systems, and it also allows for a systematic approach to the quantization of fields, which allows us to describe creation and annihilation of particles.

16.1 Lagrangian field theory

Irrespective of whether we work with relativistic or non-relativistic field theories, it is convenient to use four-dimensional notation for coordinates and partial derivatives,

$$x^\mu=\{x^0,\boldsymbol{x}\}\equiv\{ct,\boldsymbol{x}\},\quad \partial_\mu=\frac{\partial}{\partial x^\mu}=\{\partial_0,\boldsymbol{\nabla}\}.$$

We proceed by first deriving the general field equations following from a Lagrangian $\mathcal{L}(\partial\phi_I,\phi_I)$ which depends on a set of fields $\phi_I(x)\equiv\phi_I(\boldsymbol{x},t)$ and their

[1]Please review Appendix A if you are not familiar with Lagrangian mechanics, or if you need a reminder.

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first order derivatives $\partial_\mu \phi_I(x)$. These fields will be the Schrödinger field $\Psi(\boldsymbol{x}, t)$ and its complex conjugate field $\Psi^+(\boldsymbol{x}, t)$ in Chapter 17, but in Chapter 18 we will also deal with the wave function $\boldsymbol{A}(x)$ of the photon.
We know that the equations of motion for the variables $\boldsymbol{x}(t)$ of classical mechanics follow from action principles $\delta S = \delta \int dt L(\dot{\boldsymbol{x}}, \boldsymbol{x}) = 0$ in the form of the Euler-Lagrange equations

$$\frac{\partial L}{\partial x_i} - \frac{d}{dt}\frac{\partial L}{\partial \dot{x}_i} = 0.$$

The variation of a field dependent action functional

$$S[\phi] = \frac{1}{c}\int_{\mathcal{V}} d^4x\, \mathcal{L}(\partial\phi_I, \phi_I)$$

for fields $\phi_I(x)$ proceeds in the same way as in classical mechanics, the only difference being that we apply the Gauss theorem for the partial integrations. To elucidate this, we require that arbitrary first order variation

$$\phi_I(x) \to \phi_I(x) + \delta\phi_I(x)$$

with fixed fields at initial and final times t_0 and t_1,

$$\delta\phi_I(\boldsymbol{x}, t_0) = 0, \quad \delta\phi_I(\boldsymbol{x}, t_1) = 0,$$

leaves the action $S[\phi]$ in first order invariant. We also assume that the fields and their variations vanish at spatial infinity.
The first order variation of the action between the times t_0 and t_1 is

$$\begin{aligned}\delta S[\phi] &= S[\phi + \delta\phi] - S[\phi] \\ &= \int d^3\boldsymbol{x} \int_{t_0}^{t_1} dt\, [\mathcal{L}(\partial\phi_I + \partial\delta\phi_I, \phi_I + \delta\phi_I) - \mathcal{L}(\partial\phi_I, \phi_I)] \\ &= \int d^3\boldsymbol{x} \int_{t_0}^{t_1} dt \left(\delta\phi_I \frac{\partial\mathcal{L}}{\partial\phi_I} + \frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi_I)}\partial_\mu\delta\phi_I\right).\end{aligned}$$

Partial integration in the last term yields

$$\delta S[\phi] = \int d^3\boldsymbol{x} \int_{t_0}^{t_1} dt\, \delta\phi_I \left(\frac{\partial\mathcal{L}}{\partial\phi_I} - \partial_\mu \frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi_I)}\right), \tag{16.1}$$

where the boundary terms vanish because of the vanishing variations at spatial infinity and at t_0 and t_1.
Equation (16.1) implies that we can have $\delta S[\phi] = 0$ for arbitrary variations $\delta\phi_I(x)$ between t_0 and t_1 if and only if the equations

$$\frac{\partial\mathcal{L}}{\partial\phi_I} - \partial_\mu \frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi_I)} = 0 \tag{16.2}$$

hold for all the fields $\phi_I(x)$. These are the Euler-Lagrange equations for Lagrangian field theory.

The derivation of equation (16.2) does not depend on the number of four space-time dimensions, $\mu \in \{0, 1, 2, 3\}$. It would just as well go through in any number d of dimensions, where d could be a number of spatial dimensions if we study equilibrium or static phenomena in field theory, or d can be $d - 1$ spatial and one time dimension. Relevant cases for observations include $d = 1$ (mechanics or equilibrium in one-dimensional systems), $d = 2$ (equilibrium phenomena on interfaces or surfaces, time-dependent phenomena in one-dimensional systems), $d = 3$ (equilibrium phenomena in three dimensions, time-dependent phenomena on interfaces or surfaces), and $d = 4$ (time-dependent phenomena in observable spacetime). In particular, classical particle mechanics can be considered as a field theory in one spacetime dimension.

The Lagrange density for the Schrödinger field

An example is provided by the Lagrange density for the Schrödinger field,

$$\mathcal{L} = \frac{\mathrm{i}\hbar}{2}\left(\Psi^+ \cdot \frac{\partial \Psi}{\partial t} - \frac{\partial \Psi^+}{\partial t} \cdot \Psi\right) - \frac{\hbar^2}{2m} \boldsymbol{\nabla}\Psi^+ \cdot \boldsymbol{\nabla}\Psi - \Psi^+ \cdot V \cdot \Psi. \tag{16.3}$$

In the notation of the previous paragraph, this corresponds to fields $\phi_1(x) = \Psi^+(x)$ and $\phi_2(x) = \Psi(x)$, or we could also denote the real and imaginary parts of Ψ as the two fields.
We have the following partial derivatives of the Lagrange density,

$$\frac{\partial \mathcal{L}}{\partial \Psi^+} = \frac{\mathrm{i}\hbar}{2}\frac{\partial \Psi}{\partial t} - V\Psi, \quad \frac{\partial \mathcal{L}}{\partial(\partial_t \Psi^+)} = -\frac{\mathrm{i}\hbar}{2}\Psi, \quad \frac{\partial \mathcal{L}}{\partial(\partial_i \Psi^+)} = -\frac{\hbar^2}{2m}\partial_i \Psi,$$

and the corresponding adjoint equations. The Euler-Lagrange equation from variation of the action with respect to Ψ^+,

$$\frac{\partial \mathcal{L}}{\partial \Psi^+} - \partial_t \frac{\partial \mathcal{L}}{\partial(\partial_t \Psi^+)} - \partial_i \frac{\partial \mathcal{L}}{\partial(\partial_i \Psi^+)} = 0,$$

is the Schrödinger equation

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\Psi + \frac{\hbar^2}{2m}\Delta\Psi - V\Psi = 0.$$

The Euler-Lagrange equation from variation with respect to Ψ in turn yields the complex conjugate Schrödinger equation for Ψ^+. This is of course required for consistency, and is a consequence of $\mathcal{L} = \mathcal{L}^+$.
The Schrödinger field is slightly unusual in that variation of the action with respect to $\phi_1(x) = \Psi^+(x)$ yields the equation for $\phi_2(x) = \Psi(x)$ and vice versa. Generically, variation of the action with respect to a field $\phi_I(x)$ yields the equation of motion for that field[2]. However, the important conclusion from this section is that Schrödinger's quantum mechanics is a Lagrangian field theory with a Lagrange density (16.3).

[2]The unconventional behavior for the Schrödinger field can be traced back to how it arises from the Klein-Gordon or Dirac fields in the non-relativistic limit, see Chapter 21.

16.2 Symmetries and conservation laws

We consider an action with fields ϕ (ϕ_I, $1 \leq I \leq N$) in a d-dimensional space or spacetime:

$$S = \int d^d x \, \mathcal{L}(\phi, \partial\phi). \tag{16.4}$$

To reveal the connection between symmetries and conservation laws, we calculate the first order change of the action S (16.4) if we perform Transformations of the coordinates,

$$x'(x) = x - \epsilon(x). \tag{16.5}$$

This transforms the integration measure in the action as

$$d^d x' = d^d x \left(1 - \partial_\mu \epsilon^\mu\right),$$

and partial derivatives transform according to

$$\partial'_\mu = \partial_\mu + \left(\partial_\mu \epsilon^\nu\right) \partial_\nu. \tag{16.6}$$

We also include transormations of the fields,

$$\phi'(x') = \phi(x) + \delta\phi(x). \tag{16.7}$$

Coordinate transformations often also imply transformations of the fields, e.g. if ϕ is a tensor field of n-th order with components $\phi_{\alpha\ldots\nu}(x)$, the transformation induced by the coordinate transformation $x \to x'(x) = x - \epsilon(x)$ is

$$\phi'_{\alpha'\ldots\nu'}(x') = \partial_{\alpha'} x^\alpha \cdot \partial_{\beta'} x^\beta \ldots \partial_{\nu'} x^\nu \cdot \phi_{\alpha\beta\ldots\nu}(x).$$

This yields is in first order

$$\begin{aligned} \delta\phi_{\alpha\beta\ldots\nu}(x) &= \phi'_{\alpha\ldots\nu}(x') - \phi_{\alpha\ldots\nu}(x) \\ &= \partial_\alpha \epsilon^\sigma \cdot \phi_{\sigma\beta\ldots\nu}(x) + \partial_\beta \epsilon^\sigma \cdot \phi_{\alpha\sigma\ldots\nu}(x) + \ldots + \partial_\nu \epsilon^\sigma \cdot \phi_{\alpha\beta\ldots\sigma}(x). \end{aligned}$$

Fields can also transform without a coordinate transformation, e.g. through a phase transformation.
The equations (16.6) and (16.7) imply the following first order change of partial derivative terms:

$$\delta\left(\partial_\mu \phi\right) = \partial_\mu \delta\phi + \left(\partial_\mu \epsilon^\nu\right) \partial_\nu \phi. \tag{16.8}$$

The resulting first order change of the action is (with the understanding that we sum over all fields in all multiplicative terms where the field ϕ appears

twice):

$$\begin{aligned}\delta S &= \int d^d x \left[(1-\partial_\mu \epsilon^\mu)\left(\mathcal{L}+\delta\phi\frac{\partial\mathcal{L}}{\partial\phi}+\delta\left(\partial_\rho\phi\right)\frac{\partial\mathcal{L}}{\partial(\partial_\rho\phi)}-\epsilon^\sigma\delta_\sigma\mathcal{L}\right)-\mathcal{L}\right]\\ &= \int d^d x \left[(\partial_\mu\epsilon^\nu)\left(\partial_\nu\phi\cdot\frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi)}-\eta_\nu{}^\mu\mathcal{L}\right)+\partial_\mu\left(\delta\phi\frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi)}\right)\right.\\ &\quad \left.+\,\delta\phi\left(\frac{\partial\mathcal{L}}{\partial\phi}-\partial_\mu\frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi)}\right)-\epsilon^\mu\left(\partial_\mu\mathcal{L}-\partial_\mu\phi\cdot\frac{\partial\mathcal{L}}{\partial\phi}-\partial_\mu\partial_\nu\phi\cdot\frac{\partial\mathcal{L}}{\partial(\partial_\nu\phi)}\right)\right]\\ &= \int d^d x \left\{\partial_\mu\left[\epsilon^\nu\left(\partial_\nu\phi\cdot\frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi)}-\eta_\nu{}^\mu\mathcal{L}\right)+\delta\phi\frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi)}\right]\right.\\ &\quad \left.+\,(\delta\phi+\epsilon^\nu\partial_\nu\phi)\left(\frac{\partial\mathcal{L}}{\partial\phi}-\partial_\mu\frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi)}\right)\right\}. \end{aligned} \tag{16.9}$$

Here

$$\delta_\mu\mathcal{L}=\partial_\mu\mathcal{L}-\partial_\mu\phi\cdot\frac{\partial\mathcal{L}}{\partial\phi}-\partial_\mu\partial_\nu\phi\cdot\frac{\partial\mathcal{L}}{\partial(\partial_\nu\phi)}$$

is the partial derivative of $\mathcal{L}$ with respect to any *explicit* coordinate dependence. If for every integration volume, we have off-shell $\delta S\equiv 0$ for the proposed transformations ϵ, $\delta\phi$, (i.e. $\delta(d^d x\,\mathcal{L})=0$), we find a local on-shell conservation law

$$\partial_\mu j^\mu = 0 \tag{16.10}$$

with the conserved current

$$j^\mu=\epsilon^\nu\left(\eta_\nu{}^\mu\mathcal{L}-\partial_\nu\phi\cdot\frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi)}\right)-\delta\phi\frac{\partial\mathcal{L}}{\partial(\partial_\mu\phi)}. \tag{16.11}$$

The corresponding conserved charge is

$$Q=\frac{1}{c}\int d^{d-1}\boldsymbol{x}\, j^0(\boldsymbol{x},t). \tag{16.12}$$

If the off-shell variation of the action satisfies $\delta S\equiv\int d^d x\,\partial_\mu K^\mu$ for every integration volume, the on-shell conserved current is $J^\mu=j^\mu+K^\mu$ and the conserved charge is the spatial integral over J^0.

Symmetry transformations of the action which only transform the fields, but leave the coordinates invariant ($\delta\phi\neq 0$, $\epsilon=0$), are denoted as *internal symmetries*. Symmetry transformations involving coordinate transformations are denoted as *external symmetries*.

The connection between symmetries and conservation laws was developed by Emmy Noether[3] and is known as *Noether's theorem*.

[3] E. Noether, Nachr. König. Ges. Wiss. Göttingen, Math.-phys. Klasse, 235 (1918), see also arXiv:physics/0503066.

Energy-momentum tensors

We now specialize to inertial (i.e. pseudo-Cartesian) coordinates in Minkowski spacetime. If the coordinate shift in (16.5) is a constant translation, $\partial_\mu \epsilon^\nu = 0$, all fields transform like scalars, $\delta\phi = 0$, and the conserved current becomes

$$j^\mu = \epsilon^\nu \left(\eta_\nu{}^\mu \mathcal{L} - \partial_\nu \phi \cdot \frac{\partial \mathcal{L}}{\partial(\partial_\mu \phi)} \right) = \epsilon^\nu \Theta_\nu{}^\mu .$$

Omitting the d irrelevant constants ϵ^ν leaves us with d conserved currents $(0 \le \nu \le d-1)$

$$\partial_\mu \Theta_\nu{}^\mu = 0, \tag{16.13}$$

with components

$$\Theta_\nu{}^\mu = \eta_\nu{}^\mu \mathcal{L} - \partial_\nu \phi \cdot \frac{\partial \mathcal{L}}{\partial(\partial_\mu \phi)}. \tag{16.14}$$

The corresponding conserved charges

$$p_\nu = \frac{1}{c} \int d^{d-1}\boldsymbol{x}\, \Theta_\nu{}^0 \tag{16.15}$$

are the components of the four-dimensional energy-momentum vector of the physical system described by the Lagrange density $\mathcal{L}$, and the tensor with components $\Theta_\nu{}^\mu$ is therefore denoted as an *energy-momentum tensor*.
The spatial components Θ^{ij} of the energy-momentum tensor have dual interpretations in terms of momentum current densities and forces. To explain the meaning of Θ^{ij}, we pick an arbitrary (but stationary) spatial volume V. Since we are talking about fields, part of the fields will reside in V. From equation (16.15), the fields in V will carry a part of the total momentum $\boldsymbol{p}$ which is

$$\boldsymbol{p}_V = \boldsymbol{e}_i \frac{1}{c} \int_V d^{d-1}\boldsymbol{x}\, \Theta^{i0}.$$

The equations (16.13) and (16.15) imply that the change of $\boldsymbol{p}_V$ is given by

$$\frac{d}{dt}\boldsymbol{p}_V = \boldsymbol{e}_i \int_V d^{d-1}\boldsymbol{x}\, \partial_0 \Theta^{i0} = -\boldsymbol{e}_i \oint_{\partial V} d^{d-2}S_j\, \Theta^{ij}, \tag{16.16}$$

where the Gauss theorem in $d-1$ spatial dimensions was employed and $d^{d-2}S_j$ is the outward bound surface element on the boundary ∂V of the volume.
This equation tells us that the component Θ^{ij} describes the flow of the momentum component p^i through the plane with normal vector $\boldsymbol{e}_j$, i.e. Θ^{ij} is the flow of momentum p^i in the direction $\boldsymbol{e}_j$ and $\boldsymbol{j}^i = \Theta^{ij}\boldsymbol{e}_j$ is the corresponding current density. In the dual interpretation, we read equation (16.16) with the relation $\boldsymbol{F}_V = d\boldsymbol{p}_V/dt$ between force and momentum change in mind. In this interpretation, $\boldsymbol{F}_V$ *is the force exerted on the fields in the fixed volume* V, because it describes the rate of change of momentum of the fields in V. $-\boldsymbol{F}_V$

is the force exerted by the fields in the fixed volume V. The component Θ^{ij} is then the force in direction $\boldsymbol{e}_i$ per area with normal vector $\boldsymbol{e}_j$. This represents strain or pressure for $i = j$ and stress for $i \neq j$. The energy-momentum tensor is therefore also known as *stress-energy tensor*.
The energy-momentum tensor for the Schrödinger field is found by substituting (16.3) into equation (16.14). The corresponding densities of the conserved energy and momentum are usually written as a Hamiltonian density $\mathcal{H}$ and a momentum density $\boldsymbol{\mathcal{P}}$,

$$\mathcal{H} = -\Theta_0{}^0 = \frac{\hbar^2}{2m}\boldsymbol{\nabla}\Psi^+ \cdot \boldsymbol{\nabla}\Psi + \Psi^+ \cdot V \cdot \Psi, \tag{16.17}$$

$$\boldsymbol{\mathcal{P}} = \frac{1}{c}\boldsymbol{e}_i\Theta^{i0} = \frac{\hbar}{2\mathrm{i}}\left(\Psi^+ \cdot \boldsymbol{\nabla}\Psi - \boldsymbol{\nabla}\Psi^+ \cdot \Psi\right). \tag{16.18}$$

The energy $E = \int d^3\boldsymbol{x}\,\mathcal{H}$ and momentum $\boldsymbol{p} = \int d^3\boldsymbol{x}\,\boldsymbol{\mathcal{P}}$ agree with the corresponding expectation values of the Schrödinger wave function in quantum mechanics.
There is another equation for the energy-momentum tensor in general relativity, which agrees with equation (16.14) for scalar fields, but not for vector or relativistic spinor fields. Both definitions yield the same conserved energy and momentum of a system, but improvement terms have to be added to the tensor from equation (16.14) in relativistic field theories to get the correct expressions for local densities for energy and momentum.

Probability and charge conservation from invariance under phase rotations

The Lagrange density (16.3) is invariant under phase rotations of the Schrödinger field,

$$\delta\Psi(\boldsymbol{x},t) = \mathrm{i}\frac{q}{\hbar}\varphi\Psi(\boldsymbol{x},t), \quad \delta\Psi^+(\boldsymbol{x},t) = -\mathrm{i}\frac{q}{\hbar}\varphi\Psi^+(\boldsymbol{x},t).$$

We wrote the constant phase in the peculiar form $q\varphi/\hbar$ in anticipation of the connection to local gauge transformations (15.8,15.9), which will play a recurring role later on. However, for now we note that substitution of the phase transformations into the equation (16.11) yields after division by the irrelevant constant $q\varphi$ the density

$$\varrho = \frac{j^0}{c} = -\frac{1}{q\varphi}\left(\delta\Psi\frac{\partial\mathcal{L}}{\partial(\partial_t\Psi)} + \delta\Psi^+\frac{\partial\mathcal{L}}{\partial(\partial_t\Psi^+)}\right) = \Psi^+\Psi = \frac{1}{q}\varrho_q \tag{16.19}$$

and the related current density

$$\begin{aligned}\boldsymbol{j} &= -\frac{1}{q\varphi}\left(\delta\Psi\frac{\partial\mathcal{L}}{\partial(\boldsymbol{\nabla}\Psi)} + \delta\Psi^+\frac{\partial\mathcal{L}}{\partial(\boldsymbol{\nabla}\Psi^+)}\right) = \frac{\hbar}{2\mathrm{i}m}\left(\Psi^+ \cdot \boldsymbol{\nabla}\Psi - \boldsymbol{\nabla}\Psi^+ \cdot \Psi\right) \\ &= \frac{1}{q}\boldsymbol{j}_q. \end{aligned} \tag{16.20}$$

Comparison with equations (1.17) and (1.18) shows that probability conservation in Schrödinger theory can be considered as a consequence of invariance under global phase rotations.
Had we not divided out the charge q, we would have drawn the same conclusion for conservation of electric charge with $\varrho_q = q\Psi^+\Psi$ as the charge density and $\boldsymbol{j}_q = q\boldsymbol{j}$ as the electric current density. The coincidence of the conservation laws for probability and electric charge in Schrödinger theory arises because it is a theory for stable non-relativistic particles. Only charge conservation will survive in the relativistic limit, but probability conservation for particles will not hold any more, because ϱ_q will not be positive definite any more and therefore $\varrho_q(\boldsymbol{x}, t)/q$ does not yield a quantity that could be considered as a probability density to find a particle in the location $\boldsymbol{x}$ at time t.

16.3 Problems

16.1 Show that addition of any derivative term $\partial_\mu \mathcal{F}(\phi_I)$ to the Lagrange density $\mathcal{L}(\phi_I, \partial\phi_I)$ does not change the Euler-Lagrange equations.

16.2 We consider classical particle mechanics with a Lagrange function $L(q_I, \dot{q}_I)$.
2a. Suppose the action is invariant under constant shifts δq_J of the coordinate $q_J(t)$. Which conserved quantity do you find from equation (16.11)? Which condition must L fulfill to ensure that the action is not affected by the constant shift δq_J?
2b. Now we assume that the action is invariant under constant shifts $\delta t = -\epsilon$ of the internal coordinate t. Which conserved quantity do you find from equation (16.11) in this case?

16.3 We have only evaluated the components ${\Theta_0}^0$ and ${\Theta_i}^0$ of the energy-momentum tensor of the Schrödinger field in equations (16.17) and (16.18). Which energy current density $\boldsymbol{j}_\mathcal{H}$ and momentum current densities $\boldsymbol{j}^i_\mathcal{P}$ do you find from the energy-momentum tensor of the Schrödinger field?

16.4 Schrödinger fields can have different transformation properties under coordinate rotations $\delta\boldsymbol{x} = -\boldsymbol{\varphi} \times \boldsymbol{x}$, see Section 8.2. In this problem we analyze a Schrödinger field which transforms like a scalar under rotations,

$$\delta\Psi(\boldsymbol{x}, t) = \Psi'(\boldsymbol{x}', t) - \Psi(\boldsymbol{x}, t) = 0.$$

The Lagrange density (16.3) is invariant under rotations. Which conserved quantity do you find from this observation?

Solution to Problem 4

Equation (16.11) yields with $\boldsymbol{\epsilon} = \boldsymbol{\varphi} \times \boldsymbol{x}$ a conserved charge density

$$\begin{aligned}\varrho = \frac{j^0}{c} &= -(\boldsymbol{\varphi} \times \boldsymbol{x}) \cdot \left(\boldsymbol{\nabla}\Psi \frac{\partial\mathcal{L}}{\partial(\partial_t\Psi)} + \boldsymbol{\nabla}\Psi^+ \frac{\partial\mathcal{L}}{\partial(\partial_t\Psi^+)} \right) \\ &= -\frac{\mathrm{i}\hbar}{2}\boldsymbol{\varphi} \cdot \left[\boldsymbol{x} \times \left(\Psi^+ \cdot \boldsymbol{\nabla}\Psi - \boldsymbol{\nabla}\Psi^+ \cdot \Psi \right) \right] = \boldsymbol{\varphi} \cdot \boldsymbol{\mathcal{M}},\end{aligned}$$

with an angular momentum density

$$\boldsymbol{\mathcal{M}} = \frac{\hbar}{2\mathrm{i}}\boldsymbol{x} \times \left(\Psi^+ \cdot \boldsymbol{\nabla}\Psi - \boldsymbol{\nabla}\Psi^+ \cdot \Psi\right) = \boldsymbol{x} \times \boldsymbol{\mathcal{P}}. \tag{16.21}$$

Since the constant parameters $\boldsymbol{\varphi}$ are arbitrary, we find three linearly independent conserved quantities, viz. the angular momentum $\boldsymbol{M} = \int d^3\boldsymbol{x}\, \boldsymbol{\mathcal{M}} = \langle \mathbf{x} \times \mathbf{p} \rangle$ of the scalar Schrödinger field.

16.5 Now we assume that our Schrödinger field is a 2-spinor with the transformation property

$$\delta\Psi = \frac{\mathrm{i}}{2}(\boldsymbol{\varphi} \cdot \underline{\boldsymbol{\sigma}}) \cdot \Psi, \quad \delta\Psi^+ = -\frac{\mathrm{i}}{2}\Psi^+ \cdot (\boldsymbol{\varphi} \cdot \underline{\boldsymbol{\sigma}}).$$

Show that the corresponding density of "total angular momentum" of the Schrödinger field in this case consists of an orbital and a spin part,

$$\begin{aligned} \boldsymbol{\mathcal{J}} &= \frac{\hbar}{2\mathrm{i}}\boldsymbol{x} \times \left(\Psi^+ \cdot \boldsymbol{\nabla}\Psi - \boldsymbol{\nabla}\Psi^+ \cdot \Psi\right) + \frac{\hbar}{2}\Psi^+ \cdot \underline{\boldsymbol{\sigma}} \cdot \Psi \\ &= \boldsymbol{x} \times \boldsymbol{\mathcal{P}} + \Psi^+ \cdot \underline{\boldsymbol{S}} \cdot \Psi = \boldsymbol{\mathcal{M}} + \boldsymbol{\mathcal{S}}. \end{aligned} \tag{16.22}$$

Rotational invariance implies only conservation of the total angular momentum $\boldsymbol{J} = \int d^3\boldsymbol{x}\, \boldsymbol{\mathcal{J}}$. However, on the level of the Lagrange density (16.3), which does not contain spin-orbit interaction terms (8.20), the orbital and spin parts are preserved separately. We will see in Chapter 21 that spin-orbit coupling is a consequence of relativity.

Chapter 17

Non-relativistic Quantum Field Theory

Quantum mechanics, as we know it so far, deals with invariant particle numbers,

$$\frac{d}{dt}\langle\Psi(t)|\Psi(t)\rangle = 0.$$

However, at least one of the early indications of wave-particle duality implies disappearance of a particle, viz. absorption of a photon in the photoelectric effect. This reminds us of two deficiencies of Schrödinger's wave mechanics: it cannot deal with absorption or emission of particles, and it cannot deal with relativistic particles.

In the following sections we will deal with the problem of absorption and emission of particles in the non-relativistic setting, i.e. for slow electrons, protons, neutrons, or nuclei, or quasi-particles in condensed matter physics.

The strategy will be to follow a quantization procedure that works for the promotion of classical mechanics to quantum mechanics, but this time for Schrödinger theory. The correspondences will be

Classical mechanics	Schrödinger's wave mechanics
Independent variable t	Independent variables $\boldsymbol{x}, t$
Dependent variables $\boldsymbol{x}(t)$	Dependent variables $\Psi(\boldsymbol{x},t), \Psi^+(\boldsymbol{x},t)$
Newton's equation $m\ddot{\boldsymbol{x}} = -\boldsymbol{\nabla}V(\boldsymbol{x})$	Schrödinger's equation $\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\Delta\Psi + V\Psi$
Lagrangian $L = \frac{m}{2}\dot{\boldsymbol{x}}^2 - V(\boldsymbol{x})$	Lagrangian $\mathcal{L} = \frac{\mathrm{i}\hbar}{2}\left(\Psi^+\cdot\frac{\partial}{\partial t}\Psi - \frac{\partial}{\partial t}\Psi^+\cdot\Psi\right) - \frac{\hbar^2}{2m}\boldsymbol{\nabla}\Psi^+\cdot\boldsymbol{\nabla}\Psi - \Psi^+\cdot V\cdot\Psi$
Conjugate momenta $p_i(t) = \partial L/\partial\dot{x}_i(t) = m\dot{x}_i(t)$	Conjugate momenta $\Pi_\Psi(\boldsymbol{x},t) = \partial\mathcal{L}/\partial\dot{\Psi}(\boldsymbol{x},t) = \frac{\mathrm{i}\hbar}{2}\Psi^+(\boldsymbol{x},t)$, $\Pi^+_\Psi(\boldsymbol{x},t) = -\frac{\mathrm{i}\hbar}{2}\Psi(\boldsymbol{x},t)$

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and finally, promotion of the "classical" variables to operators through "canonical (anti-)commutation relations":

$$[x_i(t), p_j(t)] = \mathrm{i}\hbar\delta_{ij}, \qquad [\Psi(\boldsymbol{x}, t), \Psi^+(\boldsymbol{x}', t)]_\mp = \delta(\boldsymbol{x} - \boldsymbol{x}').$$

This procedure of promoting classical variables to operators by imposing canonical commutation or anti-commutation relations is called *canonical quantization*. Canonical quantization of fields is denoted as *field quantization*. Since the fields are often wave functions (like the Schrödinger wave function) which arose from the quantization of x and p, field quantization is sometimes also called *second quantization*.

It was clear right after the inception of quantum mechanics that the formalism was not yet capable of the description of quantum effects for photons. This led to the rapid invention of field quantization in several steps between 1925 and 1928. Key advancements[1] were the formulation of a quantum field (as a superposition of infinitely many oscillation operators) by Born, Heisenberg and Jordan in 1926, the application of infinitely many oscillation operators by Dirac in 1927 for photon emission and absorption, and the introduction of anti-commutation relations for fermionic field operators by Jordan and Wigner in 1928. Path integration over fields was introduced by Feynman in the 1940s.

17.1 Quantization of the Schrödinger field

The Lagrange density (16.3) yields the canonically conjugate momenta

$$\Pi_\Psi = \frac{\partial \mathcal{L}}{\partial \dot{\Psi}} = \frac{\mathrm{i}\hbar}{2}\Psi^+, \quad \Pi_{\Psi^+} = \frac{\partial \mathcal{L}}{\partial \dot{\Psi}^+} = -\frac{\mathrm{i}\hbar}{2}\Psi,$$

and the canonical commutation relations[2] translate for fermions (with the upper signs corresponding to anti-commutators) and bosons (with the lower signs corresponding to commutators) into

$$\begin{aligned}[\Psi(\boldsymbol{x}, t), \Psi^+(\boldsymbol{x}', t)]_\pm &\equiv \Psi(\boldsymbol{x}, t)\Psi^+(\boldsymbol{x}', t) \pm \Psi^+(\boldsymbol{x}', t)\Psi(\boldsymbol{x}, t) \\ &= \delta(\boldsymbol{x} - \boldsymbol{x}'), \end{aligned} \tag{17.1}$$

$$[\Psi(\boldsymbol{x}, t), \Psi(\boldsymbol{x}', t)]_\pm = 0, \quad [\Psi^+(\boldsymbol{x}, t), \Psi^+(\boldsymbol{x}', t)]_\pm = 0.$$

The commutation relations (17.1) in the bosonic case are like the commutation relations $[a_i, a_j^+] = \delta_{ij}$ etc. for oscillator operators. Therefore $\Psi(\boldsymbol{x}, t)$ and

[1] M. Born, W. Heisenberg & P. Jordan, Z. Phys. 35, 557 (1926); P.A.M. Dirac, Proc. Roy. Soc. London A 114, 243 (1927); P. Jordan & E. Wigner, Z. Phys. 47, 631 (1928).

[2] Recall the canonical commutation relations $[x_i(t), p_j(t)] = \mathrm{i}\hbar\delta_{ij}$, $[x_i(t), x_j(t)] = 0$, $[p_i(t), p_j(t)] = 0$ in the Heisenberg picture of quantum mechanics. It is customary to dismiss a factor of 2 in the (anti-)commutation relations (17.1), which otherwise would simply reappear in different places of the quantized Schrödinger theory.

$\Psi^+(\boldsymbol{x}', t)$ will correspond to annihilation and creation operators for particles. We will see this in detail below.
Note that $\Psi(\boldsymbol{x}, t)$ and $\Psi^+(\boldsymbol{x}, t)$ are now *time-dependent operators* and their time evolution is determined by the full dynamics of the system. Therefore they are operators in the *Heisenberg picture* of the second quantized theory, i.e. what had been representations of states in the Schrödinger picture of the first quantized theory has become field operators in the Heisenberg picture of the second quantized theory.
The Hamiltonian density is related to the Lagrange density through a Legendre transformation (cf. $H = \sum_i p_i \dot{q}_i - L$ in mechanics), $\mathcal{H} = \Pi_\Psi \dot{\Psi} + \dot{\Psi}^+ \Pi_{\Psi^+} - \mathcal{L}$. This yields the Hamiltonian $H = \int d^3\boldsymbol{x}\, \mathcal{H}$ in the form

$$H = \int d^3\boldsymbol{x} \left(\frac{\hbar^2}{2m} \boldsymbol{\nabla}\Psi^+(\boldsymbol{x}, t) \cdot \boldsymbol{\nabla}\Psi(\boldsymbol{x}, t) + \Psi^+(\boldsymbol{x}, t) V(\boldsymbol{x}) \Psi(\boldsymbol{x}, t) \right). \tag{17.2}$$

We have also found these results in equation (16.17) from the energy-momentum tensor of the Schrödinger field, which in addition gave us the momentum

$$\begin{aligned} \boldsymbol{P}(t) &= \int d^3\boldsymbol{x}\, \boldsymbol{\mathcal{P}}(\boldsymbol{x}, t) \\ &= \int d^3\boldsymbol{x}\, \frac{\hbar}{2\mathrm{i}} \left(\Psi^+(\boldsymbol{x}, t) \cdot \boldsymbol{\nabla}\Psi(\boldsymbol{x}, t) - \boldsymbol{\nabla}\Psi^+(\boldsymbol{x}, t) \cdot \Psi(\boldsymbol{x}, t) \right). \end{aligned} \tag{17.3}$$

We can also use the equivalent expressions

$$H = \int d^3\boldsymbol{x} \left(-\frac{\hbar^2}{2m} \Psi^+(\boldsymbol{x}, t) \Delta\Psi(\boldsymbol{x}, t) + \Psi^+(\boldsymbol{x}, t) \cdot V(\boldsymbol{x}) \cdot \Psi(\boldsymbol{x}, t) \right)$$

and $\boldsymbol{P}(t) = -\mathrm{i}\hbar \int d^3\boldsymbol{x}\, \Psi^+(\boldsymbol{x}, t) \boldsymbol{\nabla}\Psi(\boldsymbol{x}, t)$, which can be motivated from the corresponding equations for the energy and momentum expectation values in the first quantized Schrödinger theory.
Other frequently used operators include the number and charge operators N and Q,

$$N = \int d^3\boldsymbol{x}\, \varrho(\boldsymbol{x}, t) = \int d^3\boldsymbol{x}\, \Psi^+(\boldsymbol{x}, t) \Psi(\boldsymbol{x}, t) = \frac{1}{q} Q, \tag{17.4}$$

and the current operator

$$\boldsymbol{I}_q(t) = \int d^3\boldsymbol{x}\, \boldsymbol{j}_q(\boldsymbol{x}, t) = \frac{q}{m} \boldsymbol{P}(t).$$

The last relation follows from comparison of equation (17.3) with equation (16.20),

$$\boldsymbol{j}(\boldsymbol{x}, t) = \frac{1}{m} \boldsymbol{\mathcal{P}}(\boldsymbol{x}, t), \tag{17.5}$$

which tells us that the probability current density of the Schrödinger field is also a velocity density.

Time evolution of the field operators

The canonical (anti-)commutation relations between the field operators imply with the relations

$$\begin{aligned}[AB,C] &= ABC - CAB = ABC + ACB - ACB - CAB \\ &= A[B,C]_{\pm} - [C,A]_{\pm}B, \\ [A,BC] &= ABC - BCA = ABC + BAC - BAC - BCA \\ &= [A,B]_{\pm}C - B[C,A]_{\pm}, \end{aligned} \tag{17.6}$$

that both bosonic and fermionic field operators $\Psi(\boldsymbol{x},t)$ satisfy the Heisenberg evolution equations,

$$\frac{\partial}{\partial t}\Psi(\boldsymbol{x},t) = \mathrm{i}\frac{\hbar}{2m}\Delta\Psi(\boldsymbol{x},t) - \frac{\mathrm{i}}{\hbar}V(\boldsymbol{x})\Psi(\boldsymbol{x},t) = \frac{\mathrm{i}}{\hbar}[H,\Psi(\boldsymbol{x},t)], \tag{17.7}$$

$$\frac{\partial}{\partial t}\Psi^{+}(\boldsymbol{x},t) = -\mathrm{i}\frac{\hbar}{2m}\Delta\Psi^{+}(\boldsymbol{x},t) + \frac{\mathrm{i}}{\hbar}V(\boldsymbol{x})\Psi^{+}(\boldsymbol{x},t) = \frac{\mathrm{i}}{\hbar}[H,\Psi^{+}(\boldsymbol{x},t)]. \tag{17.8}$$

However, then we also get (note that here the time-independence of $V(\boldsymbol{x})$ is relevant)

$$\frac{d}{dt}H = \frac{\mathrm{i}}{\hbar}[H,H] = 0,$$

which was already anticipated in the notation by writing H rather than $H(t)$. The relations (17.7,17.8) confirm the Heisenberg picture interpretation of the field operators $\Psi(\boldsymbol{x},t)$ and $\Psi^{+}(\boldsymbol{x},t)$.

k-space representation of quantized Schrödinger theory

The mode expansion in the Heisenberg picture

$$\Psi(\boldsymbol{x},t) = \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\, a(\boldsymbol{k},t)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\,, \tag{17.9}$$

$$a(\boldsymbol{k},t) = \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{x}\,\Psi(\boldsymbol{x},t)\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \tag{17.10}$$

yields

$$[a(\boldsymbol{k},t), a^{+}(\boldsymbol{k}',t)]_{\pm} = \delta(\boldsymbol{k}-\boldsymbol{k}'),$$

$$[a(\boldsymbol{k},t), a(\boldsymbol{k}',t)]_{\pm} = 0, \quad [a^{+}(\boldsymbol{k},t), a^{+}(\boldsymbol{k}',t)]_{\pm} = 0.$$

Substitution of equation (17.9) into the expressions for the momentum and energy operators yields

$$\boldsymbol{P}(t) = \int d^3\boldsymbol{k}\,\hbar\boldsymbol{k}a^{+}(\boldsymbol{k},t)a(\boldsymbol{k},t) \tag{17.11}$$

and

$$H = \int d^3\boldsymbol{k}\,\frac{\hbar^2\boldsymbol{k}^2}{2m}a^+(\boldsymbol{k},t)a(\boldsymbol{k},t) + \int d^3\boldsymbol{k}\int d^3\boldsymbol{q}\,a^+(\boldsymbol{k}+\boldsymbol{q},t)V(\boldsymbol{q})a(\boldsymbol{k},t), \tag{17.12}$$

where the following normalization for the Fourier transform of single particle potentials was used,

$$V(\boldsymbol{x}) = \int d^3\boldsymbol{q}\,V(\boldsymbol{q})\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{x}),$$

$$V(\boldsymbol{q}) = V^+(-\boldsymbol{q}) = \frac{1}{(2\pi)^3}\int d^3\boldsymbol{x}\,V(\boldsymbol{x})\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{x}).$$

Field operators in the Schrödinger picture and the Fock space for the Schrödinger field

The relations in the Heisenberg picture

$$\frac{\partial}{\partial t}\Psi(\boldsymbol{x},t) = \frac{\mathrm{i}}{\hbar}[H,\Psi(\boldsymbol{x},t)], \quad \frac{\partial}{\partial t}a(\boldsymbol{k},t) = \frac{\mathrm{i}}{\hbar}[H,a(\boldsymbol{k},t)], \quad \frac{d}{dt}H = 0$$

imply

$$\Psi(\boldsymbol{x},t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)\psi(\boldsymbol{x})\exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right),$$
$$a(\boldsymbol{k},t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)a(\boldsymbol{k})\exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right).$$

The time-independent operators $\psi(\boldsymbol{x}) = \Psi(\boldsymbol{x},0)$, $a(\boldsymbol{k}) = a(\boldsymbol{k},0)$ are the corresponding operators in the *Schrödinger picture* of the quantum field theory[3]. Having time-independent operators in the Schrödinger picture comes at the expense of time-dependent states

$$|\Phi(t)\rangle = \exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right)|\Phi(0)\rangle,$$

to preserve the time dependence of matrix elements and observables. Here we use a boldface bra-ket notation $\langle\Phi|$ and $|\Phi\rangle$ for states in the second quantized theory to distinguish them from the states $\langle\Phi|$ and $|\Phi\rangle$ in the first quantized theory.

The canonical (anti-)commutation relations for the Heisenberg picture operators imply canonical (anti-)commutation relations for the Schrödinger picture operators,

$$[\psi(\boldsymbol{x}),\psi^+(\boldsymbol{x}')]_\pm = \delta(\boldsymbol{x}-\boldsymbol{x}'), \tag{17.13}$$

[3]For convenience, we have chosen the time when both pictures coincide as $t_0 = 0$.

$$
\begin{aligned}
&[\psi(\boldsymbol{x}), \psi(\boldsymbol{x}')]_{\pm} = 0, \quad [\psi^+(\boldsymbol{x}), \psi^+(\boldsymbol{x}')]_{\pm} = 0, \\
&[a(\boldsymbol{k}), a^+(\boldsymbol{k}')]_{\pm} = \delta(\boldsymbol{k} - \boldsymbol{k}'), \\
&[a(\boldsymbol{k}), a(\boldsymbol{k}')]_{\pm} = 0, \quad [a^+(\boldsymbol{k}), a^+(\boldsymbol{k}')]_{\pm} = 0.
\end{aligned} \tag{17.14}
$$

These are oscillator like commutation or anti-commutation relations, and to figure out what they mean we will look at all the composite operators of the Schrödinger field that we had constructed before.
Recall that for the single particle Hamiltonian we found the following form in terms of field operators $\Psi(\boldsymbol{x}, t)$ in the Heisenberg picture or field operators $\psi(\boldsymbol{x})$ in the Schrödinger picture,

$$
\begin{aligned}
H &= \int d^3\boldsymbol{x} \left(\frac{\hbar^2}{2m} \boldsymbol{\nabla}\Psi^+(\boldsymbol{x}, t) \cdot \boldsymbol{\nabla}\Psi(\boldsymbol{x}, t) + \Psi^+(\boldsymbol{x}, t) \cdot V(\boldsymbol{x}) \cdot \Psi(\boldsymbol{x}, t) \right) \\
&= \int d^3\boldsymbol{x} \left(\frac{\hbar^2}{2m} \boldsymbol{\nabla}\psi^+(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\psi(\boldsymbol{x}) + \psi^+(\boldsymbol{x}) \cdot V(\boldsymbol{x}) \cdot \psi(\boldsymbol{x}) \right) \\
&= \int d^3\boldsymbol{k}\, \frac{\hbar^2\boldsymbol{k}^2}{2m} a^+(\boldsymbol{k}) a(\boldsymbol{k}) + \int d^3\boldsymbol{k} \int d^3\boldsymbol{q}\, a^+(\boldsymbol{k} + \boldsymbol{q}) V(\boldsymbol{q}) a(\boldsymbol{k}).
\end{aligned} \tag{17.15}
$$

The free Hamiltonian in the Schrödinger picture is

$$
\begin{aligned}
H_0 &= \exp\left(-\frac{\mathrm{i}}{\hbar} Ht \right) \int d^3\boldsymbol{x}\, \frac{\hbar^2}{2m} \boldsymbol{\nabla}\Psi^+(\boldsymbol{x}, t) \cdot \boldsymbol{\nabla}\Psi(\boldsymbol{x}, t) \exp\left(\frac{\mathrm{i}}{\hbar} Ht \right) \\
&= \int d^3\boldsymbol{x}\, \frac{\hbar^2}{2m} \boldsymbol{\nabla}\psi^+(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\psi(\boldsymbol{x}) = \int d^3\boldsymbol{k}\, \frac{\hbar^2\boldsymbol{k}^2}{2m} a^+(\boldsymbol{k}) a(\boldsymbol{k}).
\end{aligned} \tag{17.16}
$$

The number and charge operators in the Schrödinger picture are

$$
N = \int d^3\boldsymbol{x}\, \varrho(\boldsymbol{x}) = \int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x}) \psi(\boldsymbol{x}) = \int d^3\boldsymbol{k}\, a^+(\boldsymbol{k}) a(\boldsymbol{k}) = \frac{1}{q} Q,
$$

and the current and momentum operators are

$$
\begin{aligned}
\boldsymbol{I}_q &= \int d^3\boldsymbol{x}\, \boldsymbol{j}_q(\boldsymbol{x}) = \frac{q}{m} \boldsymbol{P}, \\
\boldsymbol{P} &= \int d^3\boldsymbol{x}\, \frac{\hbar}{2\mathrm{i}} \left(\psi^+(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\psi(\boldsymbol{x}) - \boldsymbol{\nabla}\psi^+(\boldsymbol{x}) \cdot \psi(\boldsymbol{x}) \right) \\
&= \int d^3\boldsymbol{k}\, \hbar\boldsymbol{k} a^+(\boldsymbol{k}) a(\boldsymbol{k}).
\end{aligned} \tag{17.17}
$$

The momentum operator $\boldsymbol{P}(t)$ in the Heisenberg picture (17.11) is related to the momentum operator $\boldsymbol{P}$ in the Schrödinger picture through the standard transformation between Schrödinger picture and Heisenberg picture,

$$
\boldsymbol{P}(t) = \exp\left(\frac{\mathrm{i}}{\hbar} Ht \right) \boldsymbol{P} \exp\left(-\frac{\mathrm{i}}{\hbar} Ht \right),
$$

and the same similarity transformation applies to all the other operators. However, we did not write $N(t)$ or $Q(t)$ in equation (17.4), because $[H, N] = 0$ for the single particle Hamiltonian (17.15).
We are now fully prepared to identify the meaning of the operators $a(\boldsymbol{k})$ and $a^+(\boldsymbol{k})$. The commutation relations

$$[H_0, a(\boldsymbol{k})] = -\frac{\hbar^2\boldsymbol{k}^2}{2m}a(\boldsymbol{k}), \quad [H_0, a^+(\boldsymbol{k})] = \frac{\hbar^2\boldsymbol{k}^2}{2m}a^+(\boldsymbol{k}), \tag{17.18}$$

$$[\boldsymbol{P}, a(\boldsymbol{k})] = -\hbar\boldsymbol{k}a(\boldsymbol{k}), \quad [\boldsymbol{P}, a^+(\boldsymbol{k})] = \hbar\boldsymbol{k}a^+(\boldsymbol{k}), \tag{17.19}$$

$$[N, a(\boldsymbol{k})] = -a(\boldsymbol{k}), \quad [N, a^+(\boldsymbol{k})] = a^+(\boldsymbol{k}) \tag{17.20}$$

imply that $a(\boldsymbol{k})$ annihilates a particle with energy $\hbar^2\boldsymbol{k}^2/2m$, momentum $\hbar\boldsymbol{k}$, mass m and charge q, while $a^+(\boldsymbol{k})$ generates such a particle. This follows exactly in the same way as the corresponding proof for energy annihilation and creation for the harmonic oscillator (6.7-6.9). Suppose e.g. that $|\boldsymbol{K}\rangle$ is an eigenstate of the momentum operator,

$$\boldsymbol{P}|\boldsymbol{K}\rangle = \hbar\boldsymbol{K}|\boldsymbol{K}\rangle.$$

The commutation relation (17.19) then implies

$$\boldsymbol{P}a^+(\boldsymbol{k})|\boldsymbol{K}\rangle = a^+(\boldsymbol{k})\,(\boldsymbol{P} + \hbar\boldsymbol{k})\,|\boldsymbol{K}\rangle = \hbar\,(\boldsymbol{K} + \boldsymbol{k})\,a^+(\boldsymbol{k})|\boldsymbol{K}\rangle,$$

i.e.

$$a^+(\boldsymbol{k})|\boldsymbol{K}\rangle \propto |\boldsymbol{K} + \boldsymbol{k}\rangle,$$

while (17.18) implies

$$a^+(\boldsymbol{k})|E\rangle \propto |E + (\hbar^2\boldsymbol{k}^2/2m)\rangle.$$

The Hamilton operator (17.16) therefore corresponds to an infinite number of harmonic oscillators with frequencies

$$\omega(\boldsymbol{k}) = \frac{\hbar\boldsymbol{k}^2}{2m},$$

and there must exist a lowest energy state $|0\rangle$ which must be annihilated by the lowering operators,

$$a(\boldsymbol{k})|0\rangle = 0.$$

The general state then corresponds to linear superpositions of states of the form

$$|\{n_{\boldsymbol{k}}\}\rangle = \prod_{\boldsymbol{k}} \frac{a^+(\boldsymbol{k})^{n_{\boldsymbol{k}}}}{\sqrt{n_{\boldsymbol{k}}!}}|0\rangle.$$

This vector space of states is denoted as a *Fock space*.
The particle annihilation and creation interpretation of $a(\boldsymbol{k})$ and $a^+(\boldsymbol{k})$ then also implies that the Fourier component $V(\boldsymbol{q})$ in the potential term of the full Hamiltonian (17.15) shifts the momentum of a particle by $\Delta\boldsymbol{p} = \hbar\boldsymbol{q}$ by replacing a particle with momentum $\hbar\boldsymbol{k}$ with a particle of momentum $\hbar\boldsymbol{k} + \hbar\boldsymbol{q}$.

Time-dependence of H_0

The free Hamiltonian H_0 (17.16) is time-independent in the Schrödinger picture (and also in the Dirac picture introduced below), but not in the Heisenberg picture if $[H_0, H] \neq 0$. The transformation from the Schrödinger picture into the Heisenberg picture,

$$H_0(t) = \int d^3\boldsymbol{x}\, \frac{\hbar^2}{2m} \boldsymbol{\nabla}\Psi^+(\boldsymbol{x},t)\cdot\boldsymbol{\nabla}\Psi(\boldsymbol{x},t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right) H_0 \exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right),$$

implies the evolution equation

$$\begin{aligned}\frac{dH_0(t)}{dt} &= \frac{\mathrm{i}}{\hbar}[H, H_0(t)] = \frac{\mathrm{i}}{\hbar}[V(t), H_0(t)] \\ &= \frac{\mathrm{i}}{\hbar}\exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)[V, H_0]\exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right), \end{aligned} \tag{17.21}$$

The operator

$$V(t) = \int d^3\boldsymbol{x}\, \Psi^+(\boldsymbol{x},t)V(\boldsymbol{x})\Psi(\boldsymbol{x},t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right) V \exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right)$$

is the potential operator in the Heisenberg picture, while the potential operator in the Schrödinger picture is

$$V = \int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x})V(\boldsymbol{x})\psi(\boldsymbol{x}) = \int d^3\boldsymbol{k}\int d^3\boldsymbol{q}\, a^+(\boldsymbol{k}+\boldsymbol{q})V(\boldsymbol{q})a(\boldsymbol{k}).$$

The commutator in the Schrödinger picture follows from the canonical commutators or anti-commutators of the field operators as

$$[V, H_0] = \int d^3\boldsymbol{x}\, \frac{\hbar^2}{2m}\left(\psi^+(\boldsymbol{x})\cdot\boldsymbol{\nabla}\psi(\boldsymbol{x}) - \boldsymbol{\nabla}\psi^+(\boldsymbol{x})\cdot\psi(\boldsymbol{x})\right)\cdot\boldsymbol{\nabla}V(\boldsymbol{x}) \tag{17.22}$$

$$= -\int d^3\boldsymbol{k}\int d^3\boldsymbol{q}\, \frac{\hbar^2}{2m}\left(\boldsymbol{q}^2 + 2\boldsymbol{k}\cdot\boldsymbol{q}\right) a^+(\boldsymbol{k}+\boldsymbol{q})V(\boldsymbol{q})a(\boldsymbol{k}). \tag{17.23}$$

The integral in equation (17.22) contains the current density operator (1.18,16.20) of the Schrödinger field. The commutator can therefore be written as

$$[V, H_0] = \mathrm{i}\hbar\int d^3\boldsymbol{x}\, \boldsymbol{j}(\boldsymbol{x})\cdot\boldsymbol{\nabla}V(\boldsymbol{x}),$$

and substitution into the Heisenberg picture evolution equations for $H_0(t)$ (17.21) yields

$$\frac{d}{dt}H_0(t) = -\int d^3\boldsymbol{x}\, \boldsymbol{j}(\boldsymbol{x},t)\cdot\boldsymbol{\nabla}V(\boldsymbol{x}). \tag{17.24}$$

However, we have also identified $\boldsymbol{j}(\boldsymbol{x},t)$ as a velocity density operator for the Schrödinger field, cf. (17.5). The classical analog of equation (17.24) is therefore the equation for the change of the kinetic energy of a classical non-relativistic particle moving under the influence of the force $\boldsymbol{F}(\boldsymbol{x}) = -\boldsymbol{\nabla}V(\boldsymbol{x})$,

$$\frac{d}{dt}K(t) = -\boldsymbol{v}(t)\cdot\boldsymbol{\nabla}V(\boldsymbol{x}).$$

17.2 Time evolution for time-dependent Hamiltonians

The generic case in quantum field theory are time-independent Hamilton operators in the Heisenberg and Schrödinger pictures. We will see the reason for this below, after discussing the general case of a Heisenberg picture Hamiltonian $H(t) \equiv H_H(t)$ which could depend on time.
Integration of equation (17.7) yields in the general case of time-dependent $H(t)$

$$\Psi(t) = \Psi(t_0) + \frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} d\tau\,[H(\tau), \Psi(\tau)] = \tilde{U}(t, t_0)\Psi(t_0)\tilde{U}^{+}(t, t_0),$$

with the unitary operator

$$\tilde{U}(t, t_0) = \tilde{\mathrm{T}} \exp\left(\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)\right).$$

Here $\tilde{\mathrm{T}}$ locates the Hamiltonians near the upper time integration boundary leftmost, but for the factor $+\mathrm{i}$ in front of the integral.
Recall that in the Heisenberg picture, we have all time dependence in the operators, but time-independent states. To convert to the Schrödinger picture, we remove the time dependence from the operators and cast it onto the states such that matrix elements remain the same, $\langle\Phi(t_0)|\Psi(t)|\Phi(t_0)\rangle = \langle\Phi(t)|\Psi(t_0)|\Phi(t)\rangle$. The time evolution of the states in the Schrödinger picture is therefore given by

$$|\Phi(t)\rangle = \tilde{U}(t_0, t)|\Phi(t_0)\rangle. \tag{17.25}$$

This implies a Schrödinger equation

$$\begin{aligned}\mathrm{i}\hbar\frac{d}{dt}|\Phi(t)\rangle &= \tilde{U}(t_0, t)H_H(t)|\Phi(t_0)\rangle = \tilde{U}(t_0, t)H_H(t)\tilde{U}(t, t_0)|\Phi(t)\rangle \\ &= H_S(t)|\Phi(t)\rangle.\end{aligned}$$

Therefore we also have

$$|\Phi(t)\rangle = U(t, t_0)|\Phi(t_0)\rangle = \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} d\tau\, H_S(\tau)\right)|\Phi(t_0)\rangle,$$

i.e.

$$\begin{aligned}\tilde{U}(t_0, t) &= \tilde{\mathrm{T}}\exp\left(\frac{\mathrm{i}}{\hbar}\int_{t}^{t_0} d\tau\, H_H(\tau)\right) = U(t, t_0) \\ &= \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} d\tau\, H_S(\tau)\right),\end{aligned} \tag{17.26}$$

where

$$H_S(t) = \tilde{U}(t_0, t)H_H(t)\tilde{U}(t, t_0), \quad H_H(t) = U(t_0, t)H_S(t)U(t, t_0).$$

The Hamiltonian in the Schrödinger picture depends only on the t-independent field operators $\Psi(t_0)$, i.e. any time dependence of H_S can only result from an explicit time dependence of any parameter, e.g. if a coupling constant or mass would somehow depend on time. If such a time dependence through a parameter is not there, then $U(t,t_0) = \exp[-\mathrm{i}H_S(t-t_0)/\hbar]$ and $H_H(t) = H_S$, i.e. H_S is time-independent if and only if H_H is time-independent, and then $H_S = H_H$.

This explains why time-independent Hamiltonians $H_S = H_H$ are the generic case in quantum field theory. Usually, if we would discover any kind of time dependence in any parameter $\lambda = \lambda(t)$ in H_S, we would suspect that there must be a dynamical explanation in terms of a corresponding field, i.e. we would promote $\lambda(t)$ to a full dynamical field operator besides all the other field operators in H_S, including a kinetic term for $\lambda(t)$, and then the new Hamiltonian would again be time-independent.

Occasionally, we might prefer to treat a dynamical field as a given time-dependent parameter, e.g. include electric fields in a semi-classical approximation instead of dealing with the quantized photon operators. This is standard practice in the "first quantized" theory, and therefore time dependence of the Schrödinger and Heisenberg Hamiltonians plays a prominent role there. However, once we go through the hassle of field quantization, we may just as well do the same for all the fields in the theory, including electromagnetic fields, and therefore semi-classical approximations and ensuing time dependence through parameters is not as important in the second quantized theory.

17.3 The connection between first and second quantized theory

For a single particle first and second quantized theory should yield the same expectation values, i.e. matrix elements in the 1-particle sector should agree:

$$\langle\Phi|\Psi\rangle = \langle\Phi|\Psi\rangle. \tag{17.27}$$

For the states

$$|\boldsymbol{x}\rangle = \psi^+(\boldsymbol{x})|0\rangle, \quad |\boldsymbol{k}\rangle = a^+(\boldsymbol{k})|0\rangle,$$

equation (17.27) is fulfilled due to the standard Fourier transformation relation between the operators in $\boldsymbol{x}$-space and $\boldsymbol{k}$-space. The relations

$$\psi^+(\boldsymbol{x}) = \int d^3\boldsymbol{k}\, a^+(\boldsymbol{k})\langle\boldsymbol{k}|\boldsymbol{x}\rangle, \quad \psi(\boldsymbol{x}) = \int d^3\boldsymbol{k}\, \langle\boldsymbol{x}|\boldsymbol{k}\rangle a(\boldsymbol{k}),$$
$$a^+(\boldsymbol{k}) = \int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x})\langle\boldsymbol{x}|\boldsymbol{k}\rangle, \quad a(\boldsymbol{k}) = \int d^3\boldsymbol{x}\, \langle\boldsymbol{k}|\boldsymbol{x}\rangle\psi(\boldsymbol{x}),$$

yield

$$\langle \boldsymbol{x}|\boldsymbol{k}\rangle = \langle 0|\psi(\boldsymbol{x})a^+(\boldsymbol{k})|0\rangle = \int d^3\boldsymbol{k}'\,\langle \boldsymbol{x}|\boldsymbol{k}'\rangle\langle 0|a(\boldsymbol{k}')a^+(\boldsymbol{k})|0\rangle$$
$$= \int d^3\boldsymbol{k}'\,\langle \boldsymbol{x}|\boldsymbol{k}'\rangle\langle 0|[a(\boldsymbol{k}'),a^+(\boldsymbol{k})]_\pm|0\rangle = \langle \boldsymbol{x}|\boldsymbol{k}\rangle = \frac{1}{\sqrt{2\pi}^3}\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}).$$

To explore this connection further, we will use superscripts (1) and (2) to designate operators in first and second quantized theory. E.g. the 1-particle Hamiltonians in first and second quantized theory can be written as

$$H^{(1)} = \int d^3\boldsymbol{x}\,|\boldsymbol{x}\rangle\left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right)\langle \boldsymbol{x}|, \tag{17.28}$$

$$H^{(2)} = \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x})\left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right)\psi(\boldsymbol{x}). \tag{17.29}$$

We can rewrite $H^{(2)}$ as

$$H^{(2)} = \int d^3\boldsymbol{x}'\int d^3\boldsymbol{x}''\int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x}')\delta(\boldsymbol{x}'-\boldsymbol{x}'')\left(-\frac{\hbar^2}{2m}\Delta'' + V(\boldsymbol{x}'')\right)$$
$$\times\delta(\boldsymbol{x}''-\boldsymbol{x})\psi(\boldsymbol{x}) = \int d^3\boldsymbol{x}'\int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x}')\langle \boldsymbol{x}'|H^{(1)}|\boldsymbol{x}\rangle\psi(\boldsymbol{x}),$$

and again we have exact correspondence between 1-particle matrix elements in the first and second quantized theory,

$$\langle \boldsymbol{x}'|H^{(1)}|\boldsymbol{x}\rangle = \langle \boldsymbol{x}'|H^{(2)}|\boldsymbol{x}\rangle. \tag{17.30}$$

This works in general. For an operator $K^{(1)}$ from first quantized theory, the requirement of equality of 1-particle matrix elements

$$\langle \boldsymbol{k}'|K^{(2)}|\boldsymbol{k}\rangle = \langle \boldsymbol{k}'|K^{(1)}|\boldsymbol{k}\rangle, \quad \langle \boldsymbol{x}'|K^{(2)}|\boldsymbol{x}\rangle = \langle \boldsymbol{x}'|K^{(1)}|\boldsymbol{x}\rangle \tag{17.31}$$

can be solved by

$$K^{(2)} = \int d^3\boldsymbol{k}'\int d^3\boldsymbol{k}\,a^+(\boldsymbol{k}')\langle \boldsymbol{k}'|K^{(1)}|\boldsymbol{k}\rangle a(\boldsymbol{k})$$
$$= \int d^3\boldsymbol{x}'\int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x}')\langle \boldsymbol{x}'|K^{(1)}|\boldsymbol{x}\rangle\psi(\boldsymbol{x}).$$

General 1-particle states and corresponding annihilation and creation operators in second quantized theory

The equivalence of first and second quantized theory in the single-particle sector also allows us to derive the equations for 1-particle states and corresponding annihilation and creation operators in second quantization. Suppose

$|m\rangle$ and $|n\rangle$ are two states of the first quantized theory. The corresponding matrix element of the Hamiltonian in the first quantized theory is

$$\begin{aligned}
\langle m|H^{(1)}|n\rangle &= \int d^3\boldsymbol{x}\, \langle m|\boldsymbol{x}\rangle \left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right) \langle \boldsymbol{x}|n\rangle \\
&= \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \int d^3\boldsymbol{x}''\, \langle m|\boldsymbol{x}''\rangle \delta(\boldsymbol{x}''-\boldsymbol{x}) \left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right) \\
&\quad \times \delta(\boldsymbol{x}-\boldsymbol{x}')\langle \boldsymbol{x}'|n\rangle \\
&= \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \int d^3\boldsymbol{x}''\, \langle m|\boldsymbol{x}''\rangle \langle 0|\psi(\boldsymbol{x}'')\psi^+(\boldsymbol{x}) \left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x})\right) \\
&\quad \times \psi(\boldsymbol{x})\psi^+(\boldsymbol{x}')|0\rangle \langle \boldsymbol{x}'|n\rangle \\
&= \int d^3\boldsymbol{x}' \int d^3\boldsymbol{x}''\, \langle m|\boldsymbol{x}''\rangle \langle 0|\psi(\boldsymbol{x}'')H^{(2)}\psi^+(\boldsymbol{x}')|0\rangle \langle \boldsymbol{x}'|n\rangle, \qquad (17.32)
\end{aligned}$$

where we used the identity

$$\delta(\boldsymbol{x}''-\boldsymbol{x})\delta(\boldsymbol{x}-\boldsymbol{x}') = \langle 0|\psi(\boldsymbol{x}'')\psi^+(\boldsymbol{x})\psi(\boldsymbol{x})\psi^+(\boldsymbol{x}')|0\rangle$$

to write the matrix element of the 1st quantized theory as a matrix element of the 2nd quantized theory.
We can interprete the result (17.32) as equality of single particle matrix elements,

$$\langle m|H^{(1)}|n\rangle = \langle m|H^{(2)}|n\rangle$$

if we define the 1-particle states

$$|n\rangle = \int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x})|0\rangle\langle \boldsymbol{x}|n\rangle = \int d^3\boldsymbol{x}\, |\boldsymbol{x}\rangle\langle \boldsymbol{x}|n\rangle. \qquad (17.33)$$

This also motivates the definition of corresponding creation and annihilation operators

$$\begin{aligned}
a_n^+ \equiv \psi_n^+ &= \int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x})\langle \boldsymbol{x}|n\rangle = \int d^3\boldsymbol{k}\, a^+(\boldsymbol{k})\langle \boldsymbol{k}|n\rangle, \\
a_n \equiv \psi_n &= \int d^3\boldsymbol{x}\, \psi(\boldsymbol{x})\langle n|\boldsymbol{x}\rangle = \int d^3\boldsymbol{k}\, a(\boldsymbol{k})\langle n|\boldsymbol{k}\rangle.
\end{aligned}$$

E.g. the operator

$$a_{n,\ell,m}^+ \equiv \psi_{n,\ell,m}^+ = \int d^3\boldsymbol{x}\, \psi^+(\boldsymbol{x})\langle \boldsymbol{x}|n,\ell,m\rangle = \int d^3\boldsymbol{k}\, a^+(\boldsymbol{k})\langle \boldsymbol{k}|n,\ell,m\rangle$$

will create an electron in the $|n,\ell,m\rangle$ state of hydrogen. Inserting $\langle \boldsymbol{x}|n\rangle = \langle \boldsymbol{x}|n\rangle$ in equation (17.33) also shows the completeness relation in the single particle sector of the Fock space,

$$\int d^3\boldsymbol{x}\, |\boldsymbol{x}\rangle\langle \boldsymbol{x}| = 1. \qquad (17.34)$$

Time evolution of 1-particle states in second quantized theory

According to our previous observations, a state in the Schrödinger picture evolves according to

$$|\Phi(t)\rangle = \exp\left(-\frac{\mathrm{i}}{\hbar}H^{(2)}t\right)|\Phi(0)\rangle. \tag{17.35}$$

On the other hand, according to equation (17.33), a single particle state at time $t = 0$ should be given in terms of the corresponding first quantized state $|\Phi(0)\rangle$,

$$|\Phi(0)\rangle = \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x})|0\rangle\langle\boldsymbol{x}|\Phi(0)\rangle.$$

Here we wish to show that this relation is preserved under time evolution. We find from equations (17.35), (17.34) and (17.30)

$$\begin{aligned}|\Phi(t)\rangle &= \int d^3\boldsymbol{x}\,|\boldsymbol{x}\rangle\langle\boldsymbol{x}|\exp\left(-\frac{\mathrm{i}}{\hbar}H^{(2)}t\right)|\Phi(0)\rangle\\ &= \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x})|0\rangle\langle\boldsymbol{x}|\exp\left(-\frac{\mathrm{i}}{\hbar}H^{(1)}t\right)|\Phi(0)\rangle\\ &= \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x})|0\rangle\langle\boldsymbol{x}|\Phi(t)\rangle,\end{aligned}$$

i.e. the equation (17.33) is indeed preserved under time evolution of the states. We can write the Schrödinger state $|\Phi(t)\rangle$ also in the form

$$|\Phi(t)\rangle = \Phi^+(t)|0\rangle$$

with the cration operator of the particle in the first quantized state $|\Phi(t)\rangle$,

$$\Phi^+(t) = \int d^3\boldsymbol{x}\,\psi^+(\boldsymbol{x})\langle\boldsymbol{x}|\Phi(t)\rangle = \int d^3\boldsymbol{k}\,a^+(\boldsymbol{k})\langle\boldsymbol{k}|\Phi(t)\rangle. \tag{17.36}$$

Other equivalent forms of the representation of states in the Schrödinger picture involve the Heisenberg picture field operators, e.g.

$$\begin{aligned}|\Phi(t)\rangle &= \exp\left(-\frac{\mathrm{i}}{\hbar}H^{(2)}t\right)|\Phi(0)\rangle\\ &= \int d^3\boldsymbol{x}\,\exp\left(-\frac{\mathrm{i}}{\hbar}H^{(2)}t\right)\psi^+(\boldsymbol{x})|0\rangle\langle\boldsymbol{x}|\Phi(0)\rangle\\ &= \int d^3\boldsymbol{x}\,\Psi^+(\boldsymbol{x},-t)|0\rangle\langle\boldsymbol{x}|\Phi(0)\rangle\end{aligned}$$

and

$$\langle\boldsymbol{x}|\Phi(t)\rangle = \langle\boldsymbol{x}|\exp\left(-\frac{\mathrm{i}}{\hbar}H^{(2)}t\right)|\Phi(0)\rangle = \langle\boldsymbol{x},t|\Phi(0)\rangle,$$

with moving base kets

$$|\boldsymbol{x},t\rangle = \exp\left(\frac{\mathrm{i}}{\hbar}H^{(2)}t\right)|\boldsymbol{x}\rangle = \exp\left(\frac{\mathrm{i}}{\hbar}H^{(2)}t\right)\psi^+(\boldsymbol{x})|0\rangle = \Psi^+(\boldsymbol{x},t)|0\rangle,$$
$$|\boldsymbol{k},t\rangle = a^+(\boldsymbol{k},t)|0\rangle.$$

17.4 The Dirac picture in quantum field theory

Although our Hamiltonians in the Heisenberg and Schrödinger pictures are usually time-independent in quantum field theory, time-dependent perturbation theory is still used for the calculation of transition rates even with time-independent perturbations V. This will lead again to the calculation of scattering matrix elements $S_{fi} = \langle f|U_D(\infty,-\infty)|i\rangle$ of the time-evolution operator in the interaction picture. Therefore we will automatically encounter field operators in the Dirac picture, which are gotten from the time-independent field operators of the Schrödinger picture through application of an unperturbed Hamiltonian $H_0 = H - V$. In many cases this will be the free Schrödinger picture Hamiltonian

$$H_0 = \int d^3\boldsymbol{x}\,\frac{\hbar^2}{2m}\boldsymbol{\nabla}\psi^+(\boldsymbol{x})\cdot\boldsymbol{\nabla}\psi(\boldsymbol{x}) = \int d^3\boldsymbol{k}\,\frac{\hbar^2\boldsymbol{k}^2}{2m}a^+(\boldsymbol{k})a(\boldsymbol{k}).$$

Please note that the free Hamilton operator in the Heisenberg picture (we set again $t_0 = 0$ for the time when the two pictures coincide)

$$\begin{aligned} H_{0,H}(t) &= \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)H_0\exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right) \\ &= \int d^3\boldsymbol{x}\,\frac{\hbar^2}{2m}\boldsymbol{\nabla}\Psi^+(\boldsymbol{x},t)\cdot\boldsymbol{\nabla}\Psi(\boldsymbol{x},t) = \int d^3\boldsymbol{k}\,\frac{\hbar^2\boldsymbol{k}^2}{2m}a^+(\boldsymbol{k},t)a(\boldsymbol{k},t) \end{aligned}$$

usually differs from H_0, because generically

$$[H,H_0] = [V,H_0] \neq 0.$$

Transformation of the basic field operators from the Schrödinger picture into the Dirac picture yields

$$\begin{aligned} a_D(\boldsymbol{k},t) &= \exp\left(\frac{\mathrm{i}}{\hbar}H_0t\right)a(\boldsymbol{k})\exp\left(-\frac{\mathrm{i}}{\hbar}H_0t\right) = a(\boldsymbol{k})\exp\left(-\frac{\mathrm{i}\hbar}{2m}\boldsymbol{k}^2t\right) \\ &= \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{x}\,\psi(\boldsymbol{x},t)\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\,, \qquad (17.37) \\ \psi(\boldsymbol{x},t) &= \exp\left(\frac{\mathrm{i}}{\hbar}H_0t\right)\psi(\boldsymbol{x})\exp\left(-\frac{\mathrm{i}}{\hbar}H_0t\right) \\ &= \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\,a_D(\boldsymbol{k},t)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \\ &= \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\,a(\boldsymbol{k})\exp\left(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x} - \frac{\mathrm{i}\hbar}{2m}\boldsymbol{k}^2t\right). \qquad (17.38) \end{aligned}$$

Due to the simple relation (17.37) $a_D(\boldsymbol{k},t)$ is always substituted with $a(\boldsymbol{k})$ in applications of the Dirac picture.
We summarize the conventions for the notation for basic field operators in Schrödinger field theory in table 17.1.

Heisenberg picture	Schrödinger picture	Dirac picture
$\Psi(\boldsymbol{x},t)$	$\psi(\boldsymbol{x})$	$\psi(\boldsymbol{x},t)$
$\Psi^+(\boldsymbol{x},t)$	$\psi^+(\boldsymbol{x})$	$\psi^+(\boldsymbol{x},t)$
$a(\boldsymbol{k},t)$	$a(\boldsymbol{k})$	$a_D(\boldsymbol{k},t)$
$a^+(\boldsymbol{k},t)$	$a^+(\boldsymbol{k})$	$a_D^+(\boldsymbol{k},t)$

Table 17.1: Conventions for basic field operators in different pictures of Schrödinger field theory.

The Hamiltonian and the corresponding time evolution operator on the states, as well as the transition amplitudes are derived in exactly the same way as in the first quantized theory. However, these topics are important enough to warrant repetition in the framework of the second quantized theory. This time we can limit the discussion to the simpler case of time-independent Hamiltonians H and H_0 in the Schrödinger picture.
The states in the Schrödinger picture of quantum field theory satisfy the Schrödinger equation

$$\mathrm{i}\hbar\frac{d}{dt}|\Phi(t)\rangle = H|\Phi(t)\rangle,$$

which implies

$$|\Phi(t)\rangle = \exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)|\Phi(t')\rangle.$$

The transformation (17.38) $\psi(\boldsymbol{x}) \to \psi(\boldsymbol{x},t)$ into the Dirac picture implies for the states the transformation

$$|\Phi(t)\rangle \to |\Phi_D(t)\rangle = \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)|\Phi(t)\rangle.$$

The time evolution of the states in the Schrödinger picture then determines the time evolution of the states in the Dirac picture

$$\begin{aligned}|\Phi_D(t)\rangle &= \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t'\right)|\Phi_D(t')\rangle \\ &= U_D(t,t')|\Phi_D(t')\rangle\end{aligned}$$

with the time evolution operator on the states[4]

$$U_D(t,t') = \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t'\right).$$

[4]Recall that there are two time evolution operators in the Dirac picture. The free time evolution operator $U_0(t-t')$ evolves the operators $\psi(\boldsymbol{x},t) = U_0^+(t-t')\psi(\boldsymbol{x},t')U_0(t-t')$, while $U_D(t,t')$ evolves the states.

This operator satisfies the initial condition $U_D(t',t') = 1$ and the differential equations

$$\begin{aligned}
\mathrm{i}\hbar\frac{\partial}{\partial t}U_D(t,t') &= \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)(H-H_0)\exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t'\right)\\
&= \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)V\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t\right)U_D(t,t') = H_D(t)U_D(t,t'),\\
\mathrm{i}\hbar\frac{\partial}{\partial t'}U_D(t,t') &= -U_D(t,t')H_D(t'),
\end{aligned}$$

and can therefore also be written as

$$U_D(t,t') = \mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right).$$

The states in the Dirac picture therefore satisfy the Schrödinger equation

$$\mathrm{i}\hbar\frac{d}{dt}|\Phi_D(t)\rangle = H_D(t)|\Phi_D(t)\rangle$$

with the Hamiltonian

$$H_D(t) \equiv V_D(t) = \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)V\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t\right).$$

The transition amplitude from an initial unperturbed state $|\Phi_i(t')\rangle$ at time t' to a final state $|\Phi_f(t)\rangle$ at time t is

$$\begin{aligned}
S_{fi}(t,t') &= \langle\Phi_f(t)|\Phi_i(t)\rangle = \langle\Phi_f(t)|\exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)|\Phi_i(t')\rangle\\
&= \langle\Phi_f(0)|\exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t'\right)|\Phi_i(0)\rangle,
\end{aligned}$$

or with $|f\rangle \equiv |\Phi_f(0)\rangle$

$$S_{fi}(t,t') = \langle f|U_D(t,t')|i\rangle = \langle f|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t} d\tau\, H_D(\tau)\right)|i\rangle. \tag{17.39}$$

The scattering matrix $S_{fi} = \langle f|U_D(\infty,-\infty)|i\rangle$ contains information about all processes which take a physical system e.g. from an initial state $|i\rangle$ with n_i particles to a final state $|f\rangle$ with n_f. This includes in particular also processes where the interactions in $H_D(t)$ generate virtual intermediate particles which do not couple to any of the external particles. These vacuum processes need to be subtracted from the scattering matrix in each order of perturbation theory, which amounts to simply neglecting them in the evaluation of the scattering matrix. The vacuum processes also appear in the vacuum to vacuum amplitude, and the subtraction in each order of perturbation theory can also be understood as dividing the vacuum to vacuum amplitude out of the scattering matrix,

$$S_{fi} = \frac{\langle f|U_D(\infty,-\infty)|i\rangle}{\langle 0|U_D(\infty,-\infty)|0\rangle}. \tag{17.40}$$

However, unitarity of the time evolution operator $U_D(\infty,-\infty)$ implies unitarity of the scattering matrix $S_{fi} = \langle f|U_D(\infty,-\infty)|i\rangle$ as defined earlier,

$$\begin{aligned}\sum_i S_{fi}S^+_{if'} &= \sum_i S_{fi}S^*_{f'i} = \sum_i \langle f|U_D(\infty,-\infty)|i\rangle\langle f'|U_D(\infty,-\infty)|i\rangle^* \\ &= \sum_i \langle f|U_D(\infty,-\infty)|i\rangle\langle i|U^+_D(\infty,-\infty)|f'\rangle \\ &= \langle f|U_D(\infty,-\infty)U^+_D(\infty,-\infty)|f'\rangle = \delta_{ff'}.\end{aligned}$$

Therefore division by the vacuum to vacuum matrix element $\langle 0|U_D(\infty,-\infty)|0\rangle$ in the alternative definition (17.40) can only yield a unitary scattering matrix if the amplitude $\langle 0|U_D(\infty,-\infty)|0\rangle$ is a phase factor. We can understand this in the following way. Conservation laws prevent spontaneous decay of the vacuum into any excited states $|N\rangle$,

$$\langle N\neq 0|U_D(\infty,-\infty)|0\rangle = 0.$$

The completeness relation

$$|0\rangle\langle 0| + \sum_{N\neq 0}|N\rangle\langle N| = 1$$

and unitarity of the time evolution operator then implies

$$\begin{aligned}|\langle 0|U_D(\infty,-\infty)|0\rangle|^2 &= |\langle 0|U_D(\infty,-\infty)|0\rangle|^2 + \sum_{N\neq 0}|\langle N|U_D(\infty,-\infty)|0\rangle|^2 \\ &= \langle 0|U^+_D(\infty,-\infty)U_D(\infty,-\infty)|0\rangle = 1, \qquad (17.41)\end{aligned}$$

thus confirming that the vacuum to vacuum amplitude is a phase factor. We will continue to use the simpler notation $S_{fi} = \langle f|U_D(\infty,-\infty)|i\rangle$ for the scattering matrix with the understanding that we can neglect vacuum processes.

17.5 Inclusion of spin

If spin is included, the Schrödinger picture operator for creation of a particle of total spin s in the location $\boldsymbol{x}$ also carries a spin label σ, $\psi^+_\sigma(\boldsymbol{x})$. The spin label indicates the particle's spin projection in a particular direction (commonly denoted as the z axis) $s_z = \hbar\sigma$, $\sigma \equiv m_s \in \{-s, -s+1, \ldots, s\}$. The corresponding operator relations are

$$[\psi_\sigma(\boldsymbol{x}), \psi^+_{\sigma'}(\boldsymbol{x}')]_\pm = \delta_{\sigma\sigma'}\delta(\boldsymbol{x}-\boldsymbol{x}'),$$

$$[\psi_\sigma(\boldsymbol{x}), \psi_{\sigma'}(\boldsymbol{x}')]_\pm = 0, \quad [\psi^+_\sigma(\boldsymbol{x}), \psi^+_{\sigma'}(\boldsymbol{x}')]_\pm = 0,$$

with commutators for bosons (integer spin) and anti-commutators for fermions (half-integer spin).

The most common case of non-vanishing spin in non-relativistic quantum mechanics is $s = 1/2$, and then the common conventions for assigning values for the spin label σ are $1/2, +, \uparrow$ for $s_z = \hbar/2$, and $-1/2, -, \downarrow$ for $s_z = -\hbar/2$. Higher spin values can arise within non-relativistic quantum mechanics in nuclei, atoms, and molecules.
Within the framework of the "first quantized theory" a full single particle state for a particle with spin is given by

$$|\Phi(t)\rangle = \sum_\sigma \int d^3\boldsymbol{x}\, |\boldsymbol{x}, \sigma\rangle\langle \boldsymbol{x}, \sigma|\Phi(t)\rangle. \tag{17.42}$$

The meaning of the wave function is that

$$|\langle \boldsymbol{x}, \sigma|\Phi(t)\rangle|^2 = |\Phi_\sigma(\boldsymbol{x}, t)|^2$$

is a probability density to find a particle with spin projection $\hbar\sigma$ in the location $\boldsymbol{x}$ at time t, and the normalization condition is

$$\sum_\sigma \int d^3\boldsymbol{x}\, |\langle \boldsymbol{x}, \sigma|\Phi(t)\rangle|^2 = 1.$$

The Fock space creation and annihilation operators for particles in first quantized particle states $|\Phi(t)\rangle$ are then in direct generalization of (17.36)

$$\Phi^+(t) = \sum_\sigma \int d^3\boldsymbol{x}\, \psi^+_\sigma(\boldsymbol{x})\langle \boldsymbol{x}, \sigma|\Phi(t)\rangle = \sum_\sigma \int d^3\boldsymbol{k}\, a^+_\sigma(\boldsymbol{k})\langle \boldsymbol{k}, \sigma|\Phi(t)\rangle \tag{17.43}$$

and

$$\Phi(t) = \sum_\sigma \int d^3\boldsymbol{x}\, \psi_\sigma(\boldsymbol{x})\langle \Phi(t)|\boldsymbol{x}, \sigma\rangle = \sum_\sigma \int d^3\boldsymbol{k}\, a_\sigma(\boldsymbol{k})\langle \Phi(t)|\boldsymbol{k}, \sigma\rangle. \tag{17.44}$$

A single particle wave function with a set n of orbital quantum numbers and definite spin projection σ is e.g. $\langle \boldsymbol{x}, \sigma'|\Phi_{n,\sigma}(t)\rangle = \langle \boldsymbol{x}|\Phi_n(t)\rangle\delta_{\sigma\sigma'}$, and the corresponding single particle state in the quantized field theory is

$$|\Phi_{n,\sigma}(t)\rangle = \Phi^+_{n,\sigma}(t)|0\rangle = \int d^3\boldsymbol{x}\, \psi^+_\sigma(\boldsymbol{x})|0\rangle\langle \boldsymbol{x}|\Phi_n(t)\rangle.$$

A general two-particle state with particle species a and a' (e.g. an electron and a proton or two electrons) will have the form

$$\begin{aligned}|\Phi_{a,a'}(t)\rangle = {} & \frac{1}{\sqrt{1+\delta_{a,a'}}} \sum_{\sigma,\sigma'} \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}'\, \psi^+_{a,\sigma}(\boldsymbol{x})\psi^+_{a',\sigma'}(\boldsymbol{x}')|0\rangle \\ & \times\langle \boldsymbol{x}, \sigma; \boldsymbol{x}', \sigma'|\Phi_{a,a'}(t)\rangle.\end{aligned} \tag{17.45}$$

For identical particles it makes sense to require the symmetry property

$$\langle \boldsymbol{x}, \sigma; \boldsymbol{x}', \sigma' | \Phi_{a,a}(t) \rangle = \mp \langle \boldsymbol{x}', \sigma'; \boldsymbol{x}, \sigma | \Phi_{a,a}(t) \rangle, \tag{17.46}$$

with the upper sign applying to fermions and the lower sign for bosons.
In the ideal case of a completely normalizable system (e.g. two particles trapped in an oscillator potential or a box), the quantity $|\langle \boldsymbol{x}, \sigma; \boldsymbol{x}', \sigma' | \Phi_{a,a'}(t) \rangle|^2$ is a probability density for finding one particle at $\boldsymbol{x}$ with spin projection σ and the second particle at $\boldsymbol{x}'$ with spin projection σ', and we should have

$$\sum_{\sigma,\sigma'} \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \, |\langle \boldsymbol{x}, \sigma; \boldsymbol{x}', \sigma' | \Phi_{a,a'}(t) \rangle|^2 = 1$$

if we know that there is exactly one particle of kind a and one particle of kind a' in the system. It then follows with (17.46) that the state (17.45) is also normalized,

$$\langle \Phi_{a,a'}(t) | \Phi_{a,a'}(t) \rangle = 1.$$

For an example we consider a state where a particle of type a has orbital quantum numbers n and spin projection σ, and a particle of type a' has orbital quantum numbers n' and spin projection σ'. The two-particle amplitude

$$\begin{aligned} &\langle \boldsymbol{x}, \rho; \boldsymbol{x}', \rho' | \Phi_{a,n,\sigma;a',n',\sigma'}(t) \rangle = \langle \boldsymbol{x}, \rho; \boldsymbol{x}', \rho' | \Phi_{a,n,\sigma}(t), \Phi_{a',n',\sigma'}(t) \rangle \\ &\equiv \frac{\delta_{\rho,\sigma}\delta_{\rho',\sigma'} \langle \boldsymbol{x} | \Phi_{a,n}(t) \rangle \langle \boldsymbol{x}' | \Phi_{a',n'}(t) \rangle}{\sqrt{1+\delta_{a,a'}}\sqrt{1+\delta_{a,a'}\delta_{n,n'}\delta_{\sigma,\sigma'}}} \\ &\quad \mp \delta_{a,a'} \frac{\delta_{\rho',\sigma}\delta_{\rho,\sigma'} \langle \boldsymbol{x}' | \Phi_{a,n}(t) \rangle \langle \boldsymbol{x} | \Phi_{a',n'}(t) \rangle}{\sqrt{2(1+\delta_{n,n'}\delta_{\sigma,\sigma'})}} \end{aligned} \tag{17.47}$$

yields the tensor product state

$$\begin{aligned} |\Phi_{a,n,\sigma}(t), \Phi_{a',n',\sigma'}(t)\rangle = &\int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \, \psi^+_{a,\sigma}(\boldsymbol{x}) \psi^+_{a',\sigma'}(\boldsymbol{x}') |0\rangle \\ &\times \frac{\langle \boldsymbol{x} | \Phi_{a,n}(t) \rangle \langle \boldsymbol{x}' | \Phi_{a',n'}(t) \rangle}{\sqrt{1+\delta_{a,a'}\delta_{\sigma,\sigma'}\delta_{n,n'}}}. \end{aligned} \tag{17.48}$$

A two-particle state will generically *not* have the factorized form (17.48) because this form is incompatible with interactions between the two particles. We can explain this with the case of a system of two different particles that we have solved in Chapter 7. A two-particle state of a proton with quantum numbers N and an electron with quantum numbers n and definite spin projections of the two particles could be written in the form

$$|\phi_{n,\sigma}(t), \Phi_{N,\Sigma}(t)\rangle = \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \, \psi^+_{e,\sigma}(\boldsymbol{x}) \psi^+_{p,\Sigma}(\boldsymbol{x}') |0\rangle \langle \boldsymbol{x} | \phi_n(t) \rangle \langle \boldsymbol{x}' | \Phi_N(t) \rangle,$$

but we had seen in Chapter 7 that no such electron-proton state is compatible with the Coulomb interaction of the two particles. There is no solution of the

Schrödinger equation for the two particles which factorizes into the product of an electron wave function with a proton wave function. We did find factorized solutions of the form

$$\langle \boldsymbol{x}, \boldsymbol{x}'|\Phi_{\boldsymbol{K},n,\ell,m}(t)\rangle = \langle \boldsymbol{R}|\Phi_{\boldsymbol{K}}(t)\rangle\langle \boldsymbol{r}|\Phi_{n,\ell,m}(t)\rangle,$$

where the first factor

$$\langle \boldsymbol{R}|\Phi_{\boldsymbol{K}}(t)\rangle = \frac{1}{\sqrt{2\pi}^3}\exp\left(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R} - \mathrm{i}\frac{\hbar}{2m}\boldsymbol{K}^2 t\right)$$

describes center of mass motion, and the second factor

$$\langle \boldsymbol{r}|\Phi_{n,\ell,m}(t)\rangle = \langle \boldsymbol{r}|n,\ell,m\rangle\exp\left(-\frac{\mathrm{i}}{\hbar}E_n t\right)$$

describes relative motion. Therefore we can write down a two-particle state for the electron-proton system in the form

$$\begin{aligned}|\Phi_{\boldsymbol{K},n,\ell,m;\sigma,\Sigma}(t)\rangle \;=\; &\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\psi^+_{e,\sigma}(\boldsymbol{x})\psi^+_{p,\Sigma}(\boldsymbol{x}')|0\rangle\langle \boldsymbol{x}-\boldsymbol{x}'|\Phi_{n,\ell,m}(t)\rangle \\ &\times\langle (m_e\boldsymbol{x}/M) + (m_p\boldsymbol{x}'/M)|\Phi_{\boldsymbol{K}}(t)\rangle. \end{aligned} \tag{17.49}$$

I am emphasizing this to caution the reader. We frequently calculate scattering matrix elements and expectation values for many-particle states which are products of independent single-particle states like (17.48). However, we should keep in mind that these states may *temporarily* describe the state of a many-particle system, e.g. for $t \to \pm\infty$ or $t = 0$, but these tensor-product states never describe the full time evolution of many-particle systems with interactions. Two-particle systems with an interaction potential $V(\boldsymbol{x} - \boldsymbol{x}')$ (and without external fields affecting both particles differently, see Section 18.4 below) always allow for separation of the center of mass motion, and the states can be written in the form (17.49). However, the general form is (17.45). These remarks immediately generalize to N-particle states. Those states will be characterized by amplitudes $\langle \boldsymbol{x}_1,\sigma_1;\ldots;\boldsymbol{x}_N,\sigma_N|\Phi(t)\rangle$ with appropriate (anti-)symmetry properties for identical particles.

In spite of all those cautionary remarks about the limitations of tensor product states of the form (17.48) in the actual description of many-particle systems, we will now return to those states because they will help us to understand important aspects of expectation values in many-particle systems in Sections 17.6 and 17.7.

The state (17.48) is anti-symmetric or symmetric for fermions or bosons, respectively. In particular the state will vanish for identical fermions with identical spin and orbital quantum numbers $\sigma = \sigma'$, $n = n'$.

For the normalization of the state (17.48) we note that the following equations hold with upper signs for fermions,

$$\begin{aligned}\langle 0|\psi_{a',\sigma'}(\boldsymbol{y}')\psi_{a,\sigma}(\boldsymbol{y})\psi^+_{a,\sigma}(\boldsymbol{x})\psi^+_{a',\sigma'}(\boldsymbol{x}')|0\rangle \;=\; &\delta(\boldsymbol{y}-\boldsymbol{x})\delta(\boldsymbol{y}'-\boldsymbol{x}') \\ &\mp\delta_{a,a'}\delta_{\sigma,\sigma'}\delta(\boldsymbol{y}-\boldsymbol{x}')\delta(\boldsymbol{y}'-\boldsymbol{x})\end{aligned}$$

and therefore

$$\begin{aligned}
&\int d^3\boldsymbol{y}\int d^3\boldsymbol{y}'\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\langle 0|\psi_{a',\sigma'}(\boldsymbol{y}')\psi_{a,\sigma}(\boldsymbol{y})\psi^+_{a,\sigma}(\boldsymbol{x})\psi^+_{a',\sigma'}(\boldsymbol{x}')|0\rangle\\
&\quad\times\langle\Phi_{a',n'}(t)|\boldsymbol{y}'\rangle\langle\Phi_{a,n}(t)|\boldsymbol{y}\rangle\langle\boldsymbol{x}|\Phi_{a,n}(t)\rangle\langle\boldsymbol{x}'|\Phi_{a',n'}(t)\rangle\\
&=\int d^3\boldsymbol{x}\,|\langle\boldsymbol{x}|\Phi_{a,n}(t)\rangle|^2\int d^3\boldsymbol{x}'\,|\langle\boldsymbol{x}'|\Phi_{a',n'}(t)\rangle|^2\\
&\quad\mp\delta_{a,a'}\delta_{\sigma,\sigma'}\int d^3\boldsymbol{x}\,\langle\Phi_{a',n'}(t)|\boldsymbol{x}\rangle\langle\boldsymbol{x}|\Phi_{a,n}(t)\rangle\int d^3\boldsymbol{x}'\,\langle\Phi_{a,n}(t)|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|\Phi_{a',n'}(t)\rangle\\
&=1\mp\delta_{a,a'}\delta_{\sigma,\sigma'}\delta_{n,n'},
\end{aligned}$$

i.e. the 2-particle state (17.48) is properly normalized to 1, except when it vanishes because it corresponds to two fermions with identical quantum numbers. We can also form singlet states and triplet states for two spin 1/2 fermions with single-particle orbital quantum numbers n and n'. The triplet states are

$$|\Phi_{n,n';1,\pm1}(t)\rangle=|\Phi_{n,\pm1/2}(t),\Phi_{n',\pm1/2}(t)\rangle=-|\Phi_{n',n;1,\pm1}(t)\rangle, \tag{17.50}$$

$$\begin{aligned}
|\Phi_{n,n';1,0}(t)\rangle&=\frac{|\Phi_{n,1/2}(t),\Phi_{n',-1/2}(t)\rangle+|\Phi_{n,-1/2}(t),\Phi_{n',1/2}(t)\rangle}{\sqrt{2}}\\
&=-|\Phi_{n',n;1,0}(t)\rangle,
\end{aligned} \tag{17.51}$$

and the singlet state is

$$\begin{aligned}
|\Phi_{n,n';0,0}(t)\rangle&=\frac{|\Phi_{n,1/2}(t),\Phi_{n',-1/2}(t)\rangle-|\Phi_{n,-1/2}(t),\Phi_{n',1/2}(t)\rangle}{\sqrt{2}}\\
&=|\Phi_{n',n;0,0}(t)\rangle.
\end{aligned} \tag{17.52}$$

17.6 Two-particle interaction potentials and equations of motion

It is now only a small step to describe particle interactions as exchange of virtual particles between particles. We will take this step in Section 19.7 for exchange of non-relativistic virtual particles, and in Chapter 18 for photon exchange between charged particles. However, a description of interactions through 2-particle interaction potentials V is often sufficient. Furthermore, interaction potentials also appear in quantum electrodynamics in the Coulomb gauge.

The Hamiltonian with stationary particle-particle interaction potentials $V_{a,a'}(\boldsymbol{x})$

has the same form in the Schrödinger picture and in the Heisenberg picture,

$$H = \frac{1}{2}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\sum_{a,a'}\sum_{\sigma,\sigma'}\psi^+_{a,\sigma}(\boldsymbol{x})\psi^+_{a',\sigma'}(\boldsymbol{x}')V_{a,a'}(\boldsymbol{x}-\boldsymbol{x}')\psi_{a',\sigma'}(\boldsymbol{x}')\psi_{a,\sigma}(\boldsymbol{x})$$
$$+\int d^3\boldsymbol{x}\sum_{a,\sigma}\frac{\hbar^2}{2m_a}\boldsymbol{\nabla}\psi^+_{a,\sigma}(\boldsymbol{x})\cdot\boldsymbol{\nabla}\psi_{a,\sigma}(\boldsymbol{x}) \tag{17.53}$$
$$= \frac{1}{2}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\sum_{a,a'}\sum_{\sigma,\sigma'}\Psi^+_{a,\sigma}(\boldsymbol{x},t)\Psi^+_{a',\sigma'}(\boldsymbol{x}',t)V_{a,a'}(\boldsymbol{x}-\boldsymbol{x}')$$
$$\times\Psi_{a',\sigma'}(\boldsymbol{x}',t)\Psi_{a,\sigma}(\boldsymbol{x},t)$$
$$+\int d^3\boldsymbol{x}\sum_{a,\sigma}\frac{\hbar^2}{2m_a}\boldsymbol{\nabla}\Psi^+_{a,\sigma}(\boldsymbol{x},t)\cdot\boldsymbol{\nabla}\Psi_{a,\sigma}(\boldsymbol{x},t). \tag{17.54}$$

If the operators $\psi^+_{1,\sigma}(\boldsymbol{x})$ describe electrons, we would include e.g. the repulsive Coulomb potential $V_{11}(\boldsymbol{x}-\boldsymbol{x}') = e^2/(4\pi\epsilon_0|\boldsymbol{x}-\boldsymbol{x}'|)$ between pairs of electrons. The ordering of annihilation and creation operators in the potential term in equation (17.53) is determined by the requirement that the expectation value of the interaction potential for the vacuum $|0\rangle$ and for single particle states $|\Phi_n(t)\rangle$ vanishes. The nested structure $\psi^+_{a,\sigma}(\boldsymbol{x})\psi^+_{a',\sigma'}(\boldsymbol{x}')\psi_{a',\sigma'}(\boldsymbol{x}')\psi_{a,\sigma}(\boldsymbol{x})$ of the operators ensures the correct sign for the interaction energy of two-fermion states.

It is also instructive to write the Hamiltonian (17.53) in wavevector space. We find with

$$V(\boldsymbol{x}) = \int d^3\boldsymbol{q}\, V(\boldsymbol{q})\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{x}),$$

$$V(\boldsymbol{q}) = V^+(-\boldsymbol{q}) = \frac{1}{(2\pi)^3}\int d^3\boldsymbol{x}\, V(\boldsymbol{x})\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{x})$$

the representations

$$H = \frac{1}{2}\int d^3\boldsymbol{k}\int d^3\boldsymbol{k}'\int d^3\boldsymbol{q}\sum_{\sigma,\sigma'}a^+_\sigma(\boldsymbol{k}+\boldsymbol{q})a^+_{\sigma'}(\boldsymbol{k}'-\boldsymbol{q})V(\boldsymbol{q})a_{\sigma'}(\boldsymbol{k}')a_\sigma(\boldsymbol{k})$$
$$+\int d^3\boldsymbol{k}\sum_\sigma\frac{\hbar^2\boldsymbol{k}^2}{2m}a^+_\sigma(\boldsymbol{k})a_\sigma(\boldsymbol{k}) \tag{17.55}$$
$$= \frac{1}{2}\int d^3\boldsymbol{k}\int d^3\boldsymbol{k}'\int d^3\boldsymbol{q}\sum_{\sigma,\sigma'}a^+_\sigma(\boldsymbol{k}+\boldsymbol{q},t)a^+_{\sigma'}(\boldsymbol{k}'-\boldsymbol{q},t)V(\boldsymbol{q})$$
$$\times a_{\sigma'}(\boldsymbol{k}',t)a_\sigma(\boldsymbol{k},t)+\int d^3\boldsymbol{k}\sum_\sigma\frac{\hbar^2\boldsymbol{k}^2}{2m}a^+_\sigma(\boldsymbol{k},t)a_\sigma(\boldsymbol{k},t), \tag{17.56}$$

where the labels a and a' for the particle species are suppressed. The representations in momentum space imply that the Fourier component $V(\boldsymbol{q})$ of the two-particle interaction potential describes exchange of momentum $\hbar\boldsymbol{q}$ between the two interacting particles. Note that symmetric interaction potentials

$V(\boldsymbol{x}) = V(-\boldsymbol{x})$ are also symmetric in wavevector space $V(\boldsymbol{q}) = V(-\boldsymbol{q})$. The Coulomb potential e.g. is dominated by small momentum exchange, $V(\boldsymbol{q}) = (2\pi)^{-3}(e^2/\epsilon_0)\boldsymbol{q}^{-2}$.
The corresponding Hamiltonians in the Dirac picture are

$$\begin{aligned} H_0 &= \int d^3\boldsymbol{x} \sum_\sigma \frac{\hbar^2}{2m} \boldsymbol{\nabla}\psi_\sigma^+(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\psi_\sigma(\boldsymbol{x}) = \int d^3\boldsymbol{k} \sum_\sigma \frac{\hbar^2\boldsymbol{k}^2}{2m} a_\sigma^+(\boldsymbol{k}) a_\sigma(\boldsymbol{k}) \\ &= \int d^3\boldsymbol{x} \sum_\sigma \frac{\hbar^2}{2m} \boldsymbol{\nabla}\psi_\sigma^+(\boldsymbol{x},t) \cdot \boldsymbol{\nabla}\psi_\sigma(\boldsymbol{x},t) \\ &= \int d^3\boldsymbol{k} \sum_\sigma \frac{\hbar^2\boldsymbol{k}^2}{2m} a_{D,\sigma}^+(\boldsymbol{k},t) a_{D,\sigma}(\boldsymbol{k},t) \end{aligned}$$

and

$$\begin{aligned} H_D(t) &= \exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right)(H - H_0)\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t\right) \\ &= \frac{1}{2}\int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \sum_{\sigma,\sigma'} \psi_\sigma^+(\boldsymbol{x},t)\psi_{\sigma'}^+(\boldsymbol{x}',t) V(\boldsymbol{x}-\boldsymbol{x}')\psi_{\sigma'}(\boldsymbol{x}',t)\psi_\sigma(\boldsymbol{x},t) \\ &= \frac{1}{2}\int d^3\boldsymbol{k} \int d^3\boldsymbol{k}' \int d^3\boldsymbol{q} \sum_{\sigma,\sigma'} a_{D,\sigma}^+(\boldsymbol{k}+\boldsymbol{q},t) a_{D,\sigma'}^+(\boldsymbol{k}'-\boldsymbol{q},t) V(\boldsymbol{q}) \\ &\quad \times a_{D,\sigma'}(\boldsymbol{k}',t) a_{D,\sigma}(\boldsymbol{k},t), \end{aligned}$$

with the time-dependent field operators in the Dirac picture. Recall that H_0 determines the time evolution of the operators, while $H_D(t)$ determines the time evolution of the states in the Dirac picture.
Contrary to H_0, we cannot simply replace the time-dependent field operators in the Dirac picture with the time-independent operators of the Schrödinger picture in $H_D(t)$, because $[H_0, V] \neq 0$. In applications within non-relativistic field theory one often uses the representation $H_D(t) = \exp(\mathrm{i}H_0 t/\hbar) V \exp(-\mathrm{i}H_0 t/\hbar)$, where the Schrödinger picture potential operator V is given in terms of the time-independent field operators.

Equation of motion

The derivation of the equation of motion for the Schrödinger picture state (17.45) with the Schrödinger picture Hamiltonian (17.53) is easily done with the relation

$$\begin{aligned} &\psi_{\rho'}(\boldsymbol{y}')\psi_\rho(\boldsymbol{y})\psi_\sigma^+(\boldsymbol{x})\psi_{\sigma'}^+(\boldsymbol{x}')|0\rangle = [\psi_{\rho'}(\boldsymbol{y}'), [\psi_\rho(\boldsymbol{y}), \psi_\sigma^+(\boldsymbol{x})\psi_{\sigma'}^+(\boldsymbol{x}')]_-]_\pm|0\rangle \\ &= \delta_{\rho\sigma}\delta(\boldsymbol{x}-\boldsymbol{y})\delta_{\rho'\sigma'}\delta(\boldsymbol{x}'-\boldsymbol{y}')|0\rangle \mp \delta_{\rho\sigma'}\delta(\boldsymbol{x}'-\boldsymbol{y})\delta_{\rho'\sigma}\delta(\boldsymbol{x}-\boldsymbol{y}')|0\rangle, \end{aligned}$$

with the upper signs for fermions. This yields both for bosons and fermions the equation

$$\begin{aligned}
&\mathrm{i}\hbar\frac{d}{dt}|\Phi_{a,a'}(t)\rangle = H|\Phi_{a,a'}(t)\rangle \\
&= \frac{1}{\sqrt{1+\delta_{a,a'}}}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\sum_{\sigma,\sigma'}\psi^+_{a,\sigma}(\boldsymbol{x})\psi^+_{a',\sigma'}(\boldsymbol{x}')|0\rangle \\
&\quad\times\left(-\frac{\hbar^2}{2m_a}\Delta-\frac{\hbar^2}{2m_{a'}}\Delta'+V_{a,a'}(\boldsymbol{x}-\boldsymbol{x}')\right)\langle\boldsymbol{x},\sigma;\boldsymbol{x}',\sigma'|\Phi_{a,a'}(t)\rangle. \qquad (17.57)
\end{aligned}$$

Here we used $\Delta \equiv \partial^2/\partial\boldsymbol{x}^2$, $\Delta' \equiv \partial^2/\partial\boldsymbol{x}'^2$ and symmetry of the potential: $V_{a,a'}(\boldsymbol{x}-\boldsymbol{x}') = V_{a',a}(\boldsymbol{x}'-\boldsymbol{x})$.
Linear independence of the states $\psi^+_\sigma(\boldsymbol{x})\psi^+_{\sigma'}(\boldsymbol{x}')|0\rangle$ (or equivalently application of the projector $\langle 0|\psi_{a',\rho'}(\boldsymbol{y}')\psi_{a,\rho}(\boldsymbol{y})$ and the symmetry property (17.46)) implies that equation (17.57) is equivalent to the two-particle Schrödinger equation

$$\begin{aligned}
\mathrm{i}\hbar\frac{\partial}{\partial t}\langle\boldsymbol{x},\sigma;\boldsymbol{x}',\sigma'|\Phi_{a,a'}(t)\rangle &= \left(-\frac{\hbar^2}{2m_a}\Delta-\frac{\hbar^2}{2m_{a'}}\Delta'+V_{a,a'}(\boldsymbol{x}-\boldsymbol{x}')\right) \\
&\quad\times\langle\boldsymbol{x},\sigma;\boldsymbol{x}',\sigma'|\Phi_{a,a'}(t)\rangle. \qquad (17.58)
\end{aligned}$$

Time-independence of the Hamiltonian implies that we can also write this in the time-independent form

$$\begin{aligned}
E\langle\boldsymbol{x},\sigma;\boldsymbol{x}',\sigma'|\Phi_{a,a'}\rangle &= \left(-\frac{\hbar^2}{2m_a}\Delta-\frac{\hbar^2}{2m_{a'}}\Delta'+V_{a,a'}(\boldsymbol{x}-\boldsymbol{x}')\right) \\
&\quad\times\langle\boldsymbol{x},\sigma;\boldsymbol{x}',\sigma'|\Phi_{a,a'}\rangle. \qquad (17.59)
\end{aligned}$$

These are exactly the two-particle Schrödinger equations that we would have expected for a wave function which describes two particles interacting with a potential V. Indeed, we have used this expectation already in Chapter 7 to formulate the equation of motion for the electron-proton system that constitutes a hydrogen atom. The not entirely trivial observation at this point is that these two-particle Schrödinger equations also holds for identical particles. The only manifestation of statistics of the particles is the symmetry property (17.46) of the two-particle wave function[5].

[5] *Formal* substitution e.g. of two-particle tensor product states of definite spin for two identical particles,

$$\langle\boldsymbol{x},\sigma;\boldsymbol{x}',\sigma'|\Phi_{n,n'}\rangle = \frac{\langle\boldsymbol{x}|\Phi_n\rangle\langle\boldsymbol{x}'|\Phi_{n'}\rangle \mp \delta_{\sigma,\sigma'}\langle\boldsymbol{x}|\Phi_{n'}\rangle\langle\boldsymbol{x}'|\Phi_n\rangle}{\sqrt{2(1+\delta_{n,n'}\delta_{\sigma,\sigma'})}} \qquad (17.60)$$

(cf. equation (17.47) for $a=a'$, $\rho=\sigma$, $\rho'=\sigma'$) and projection onto effective single particle equations using orthonormality of single particle wave functions yields exchange terms. However, the resulting equations are not identical with the Hartree-Fock equations from problem 17.6, because E in equation (17.59) is the total energy of the system, whereas the Lagrange multipliers ϵ_n in Hartree-Fock equations do not add up to the total energy of a many particle system, see problem 17.6b. The formal nature of the substitution (17.60) is emphasized because we know that solutions of equation (17.59) do not factorize in single particle tensor products.

17.7 Expectation values and exchange terms

It is not difficult to discuss expectation values for the general two-particle state (17.45). However, it is more instructive to do this for the tensor product of single-particle states (17.48) with $a = a'$.
The result for the kinetic Hamiltonian in the Schrödinger picture

$$H_0|\Phi_{n,\sigma}(t),\Phi_{n',\sigma'}(t)\rangle = \frac{1}{\sqrt{1+\delta_{\sigma\sigma'}\delta_{nn'}}}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\psi^+_\sigma(\boldsymbol{x})\psi^+_{\sigma'}(\boldsymbol{x}')|0\rangle$$
$$\times\left(-\frac{\hbar^2}{2m}\Delta\langle\boldsymbol{x}|\Phi_n(t)\rangle\langle\boldsymbol{x}'|\Phi_{n'}(t)\rangle - \frac{\hbar^2}{2m}\langle\boldsymbol{x}|\Phi_n(t)\rangle\Delta'\langle\boldsymbol{x}'|\Phi_{n'}(t)\rangle\right)$$

also immediately yields the expectation value of the kinetic energy operator in the two-particle state (17.48),

$$\begin{aligned}\langle H_0\rangle &= \langle\Phi_{n,\sigma}(t),\Phi_{n',\sigma'}(t)|H_0|\Phi_{n,\sigma}(t),\Phi_{n',\sigma'}(t)\rangle = -\frac{\hbar^2}{2m(1+\delta_{\sigma\sigma'}\delta_{nn'})}\\
&\quad\times\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\Big(\langle\Phi_{n'}(t)|\boldsymbol{x}'\rangle\langle\Phi_n(t)|\boldsymbol{x}\rangle\Delta\langle\boldsymbol{x}|\Phi_n(t)\rangle\langle\boldsymbol{x}'|\Phi_{n'}(t)\rangle\\
&\quad+\langle\Phi_{n'}(t)|\boldsymbol{x}'\rangle\langle\Phi_n(t)|\boldsymbol{x}\rangle\langle\boldsymbol{x}|\Phi_n(t)\rangle\Delta'\langle\boldsymbol{x}'|\Phi_{n'}(t)\rangle\\
&\quad\mp\delta_{\sigma\sigma'}\langle\Phi_{n'}(t)|\boldsymbol{x}\rangle\langle\Phi_n(t)|\boldsymbol{x}'\rangle\Delta\langle\boldsymbol{x}|\Phi_n(t)\rangle\langle\boldsymbol{x}'|\Phi_{n'}(t)\rangle\\
&\quad\mp\delta_{\sigma\sigma'}\langle\Phi_{n'}(t)|\boldsymbol{x}\rangle\langle\Phi_n(t)|\boldsymbol{x}'\rangle\langle\boldsymbol{x}|\Phi_n(t)\rangle\Delta'\langle\boldsymbol{x}'|\Phi_{n'}(t)\rangle\Big)\\
&= \frac{1\mp\delta_{\sigma\sigma'}\delta_{nn'}}{1+\delta_{\sigma\sigma'}\delta_{nn'}}K_{nn'},\end{aligned}$$

i.e. unless the two-particle state vanishes because it describes two fermions with identical quantum numbers, the kinetic energy is the sum of the kinetic energies in the orbital motion of the two particles,

$$\begin{aligned}K_{nn'} &= \langle\Phi_{n,\sigma}(t),\Phi_{n',\sigma'}(t)|H_0|\Phi_{n,\sigma}(t),\Phi_{n',\sigma'}(t)\rangle\Big|_{(n,\sigma)\neq(n',\sigma')\text{ for fermions}}\\
&= -\int d^3\boldsymbol{x}\,\frac{\hbar^2}{2m}\Big(\langle\Phi_n(t)|\boldsymbol{x}\rangle\Delta\langle\boldsymbol{x}|\Phi_n(t)\rangle + \langle\Phi_{n'}(t)|\boldsymbol{x}\rangle\Delta\langle\boldsymbol{x}|\Phi_{n'}(t)\rangle\Big).\end{aligned}$$

The potential operator in the Schrödinger picture

$$V = \frac{1}{2}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\sum_{\sigma,\sigma'}\psi^+_\sigma(\boldsymbol{x})\psi^+_{\sigma'}(\boldsymbol{x}')V(\boldsymbol{x}-\boldsymbol{x}')\psi_{\sigma'}(\boldsymbol{x}')\psi_\sigma(\boldsymbol{x})$$

satisfies with $V(\boldsymbol{x}-\boldsymbol{x}') = V(\boldsymbol{x}'-\boldsymbol{x})$ both for fermions and for bosons the equation

$$\begin{aligned}V|\Phi_{n,\sigma}(t),\Phi_{n',\sigma'}(t)\rangle &= \frac{1}{\sqrt{1+\delta_{\sigma\sigma'}\delta_{nn'}}}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\psi^+_\sigma(\boldsymbol{x})\psi^+_{\sigma'}(\boldsymbol{x}')|0\rangle\\
&\quad\times V(\boldsymbol{x}-\boldsymbol{x}')\langle\boldsymbol{x}|\Phi_n(t)\rangle\langle\boldsymbol{x}'|\Phi_{n'}(t)\rangle\Big).\end{aligned}$$

This yields again with upper signs for fermions the result

$$\begin{aligned}\langle V\rangle &= \langle \Phi_{n,\sigma}(t), \Phi_{n',\sigma'}(t)|V|\Phi_{n,\sigma}(t), \Phi_{n',\sigma'}(t)\rangle \\ &= \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \, \frac{V(\boldsymbol{x}-\boldsymbol{x}')}{1+\delta_{nn'}\delta_{\sigma\sigma'}} \Big(\langle\Phi_n(t)|\boldsymbol{x}\rangle\langle\Phi_{n'}(t)|\boldsymbol{x}'\rangle\langle\boldsymbol{x}|\Phi_n(t)\rangle\langle\boldsymbol{x}'|\Phi_{n'}(t)\rangle \\ &\quad \mp\delta_{\sigma\sigma'}\langle\Phi_n(t)|\boldsymbol{x}\rangle\langle\Phi_{n'}(t)|\boldsymbol{x}'\rangle\langle\boldsymbol{x}'|\Phi_n(t)\rangle\langle\boldsymbol{x}|\Phi_{n'}(t)\rangle\Big),\end{aligned}$$

i.e. the expectation value for the potential energy becomes

$$\begin{aligned}\langle V\rangle &= \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \, \Phi_n^+(\boldsymbol{x},t)\Phi_n(\boldsymbol{x},t)\frac{V(\boldsymbol{x}-\boldsymbol{x}')}{1+\delta_{nn'}\delta_{\sigma\sigma'}}\Phi_{n'}^+(\boldsymbol{x}',t)\Phi_{n'}(\boldsymbol{x}',t) \\ &\quad \mp\delta_{\sigma\sigma'}\int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \, \Phi_n^+(\boldsymbol{x},t)\Phi_{n'}(\boldsymbol{x},t)\frac{V(\boldsymbol{x}-\boldsymbol{x}')}{1+\delta_{nn'}}\Phi_{n'}^+(\boldsymbol{x}',t)\Phi_n(\boldsymbol{x}',t).\end{aligned}$$

We can collect the results for the expectation values of kinetic and potential energy of the two-particle state (17.48) (with upper signs for fermions)

$$\begin{aligned}\langle H\rangle &= \langle \Phi_{n,\sigma}(t), \Phi_{n',\sigma'}(t)|H|\Phi_{n,\sigma}(t), \Phi_{n',\sigma'}(t)\rangle \\ &= \frac{1\mp\delta_{\sigma\sigma'}\delta_{nn'}}{1+\delta_{\sigma\sigma'}\delta_{nn'}}K_{nn'} + \frac{C_{nn'}\mp J_{nn'}\delta_{\sigma\sigma'}}{1+\delta_{\sigma\sigma'}\delta_{nn'}},\end{aligned} \tag{17.61}$$

with the Coulomb term[6]

$$C_{nn'} = \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \, \Phi_n^+(\boldsymbol{x},t)\Phi_{n'}^+(\boldsymbol{x}',t)V(\boldsymbol{x}-\boldsymbol{x}')\Phi_{n'}(\boldsymbol{x}',t)\Phi_n(\boldsymbol{x},t) \tag{17.62}$$

and the *exchange integral*[7]

$$J_{nn'} = \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \, \Phi_{n'}^+(\boldsymbol{x},t)\Phi_n^+(\boldsymbol{x}',t)V(\boldsymbol{x}-\boldsymbol{x}')\Phi_{n'}(\boldsymbol{x}',t)\Phi_n(\boldsymbol{x},t). \tag{17.63}$$

The Coulomb term is what we would have expected for the energy of the interaction of two particles with quantum numbers n and n'. The exchange interaction, on the other hand, is a pure quantum effect which only exists as a consequence of the canonical (anti-)commutation relations for bosonic or fermionic operators. In the first quantized theory it appears as a consequence of symmetrized boson wave functions and anti-symmetrized fermion wave functions.

For electrons with aligned spins (17.50) and also for the $m = 0$ triplet state (17.51) we must have $n \neq n'$, and the result (17.61) implies a shift of the ordinary Coulomb term $C_{nn'}$ by the exchange term $J_{nn'}$, $C_{nn'} \to C_{nn'} - J_{nn'}$. For the $m = 0$ triplet state the exchange integral arises from the cross multiplication terms in the evaluation of the expectation value. By the same token, the

[6] As derived, this result applies to every 2-particle interaction potential. The most often studied case in atomic, molecular and condensed matter physics is the Coulomb interaction between electrons, and therefore the standard (non-exchange) interaction term is simply denoted as the Coulomb term.

[7] W. Heisenberg, Z. Phys. 38, 411 (1926); Z. Phys. 39, 499 (1926).

Coulomb term for the singlet state (17.52) gets shifted to $(C_{nn'}+J_{nn'})/(1+\delta_{nn'})$ due to the cross multiplication terms. The potential energy part of the Hamiltonian (17.53) can therefore be replaced by an effective spin interaction Hamiltonian[8] (with dimensionless spins: $\boldsymbol{S}/\hbar \to \boldsymbol{S}$)

$$\begin{aligned} H_{nn'} &= \frac{1}{1+\delta_{nn'}}\left(C_{nn'} + J_{nn'} - J_{nn'}(\boldsymbol{S}+\boldsymbol{S}')^2\right) \\ &= \frac{1}{1+\delta_{nn'}}\left(C_{nn'} - \frac{1}{2}J_{nn'}(1+4\boldsymbol{S}\cdot\boldsymbol{S}')\right), \end{aligned} \tag{17.64}$$

where $\boldsymbol{S}$ and $\boldsymbol{S}'$ are the dimensionless spin operators for two electrons. Equation (17.64) gives the correct shifts by $\mp J_{nn'}$ because $(\boldsymbol{S}+\boldsymbol{S}')^2 = 2$, $\boldsymbol{S}\cdot\boldsymbol{S}' = 1/4$, in the triplet state and $(\boldsymbol{S}+\boldsymbol{S}')^2 = 0$, $\boldsymbol{S}\cdot\boldsymbol{S}' = -3/4$, in the singlet state. Note that $C_{nn} = J_{nn}$, and therefore

$$\frac{C_{nn'} - J_{nn'}}{1+\delta_{nn'}} = C_{nn'} - J_{nn'}.$$

The Hamiltonian (17.64) without the constant terms is known as the Heisenberg Hamiltonian[9].

Equations (17.61) and (17.64) show that the Coulomb interaction between electrons, through the exchange integral, effectively generates an interaction of the same form as the magnetic spin-spin interaction. The exchange interaction usually dominates over the magnetic spin-spin interaction in materials. For example in atoms or molecules $J_{nn'}$ will be of order of a few eV, whereas the energy of the genuine magnetic dipole-dipole interaction will only be of order meV or smaller. Exchange interaction with $J_{nn'} > 0$ therefore can align electron spins to generate ferromagnetism[10], but the magnetic dipole interaction will certainly not accomplish this at room temperature.

17.8 From many particle theory to second quantization

Second quantization (or field quantization) of the Schrödinger field is relevant for condensed matter physics and statistical physics, but it is usually not introduced through quantization of the corresponding Lagrangian field theory. An alternative approach proceeds through the observation that field quantization yields the same matrix elements as symmetrized wave functions (for bosons) or

[8] P.A.M. Dirac, Proc. Roy. Soc. London A 123, 714 (1929).

[9] Heisenberg had introduced exchange integrals in 1926, and he published an investigation of ferromagnetism based on the exchange interaction (17.61) in 1928 (Z. Phys. 49, 619 (1928)). However, the effective Hamiltonian (17.64) was introduced by Dirac in the previously mentioned reference in 1929. Therefore a better name for (17.64) would be Dirac-Heisenberg Hamiltonian.

[10] Ferromagnetism or anti-ferromagnetism in magnetic materials usually requires indirect exchange interactions, see e.g. [4, 11, 20, 38].

anti-symmetrized wave functions (for fermions) in first quantized theory with a fixed number N of particles.
In short this reasoning goes as follows. We assume a finite volume $V = L^3$ of our system. Then we can restrict attention to discrete momenta

$$\boldsymbol{k} = \frac{2\pi}{L}\boldsymbol{n}, \;\; \boldsymbol{n} \in \mathbb{N}^3,$$

and the N-particle momentum eigenstates are generated by states of the form

$$|\boldsymbol{k}_1, \dots \boldsymbol{k}_N\rangle = |\boldsymbol{k}_1\rangle \dots |\boldsymbol{k}_N\rangle.$$

This state needs to be symmetrized for indistinguishable bosons by summing over all $N!$ permutations P of the N momenta,

$$\sum_{P\in S_N} P|\boldsymbol{k}_1, \dots \boldsymbol{k}_N\rangle$$

However, this state is not generically normalized. If the momentum $\boldsymbol{k}$ is realized $n_{\boldsymbol{k}}$ times in the state, then

$$\left|\sum_{P\in S_N} P|\boldsymbol{k}_1, \dots \boldsymbol{k}_N\rangle\right|^2 = \frac{N!}{\prod_{\boldsymbol{k}} n_{\boldsymbol{k}}!}\left(\prod_{\boldsymbol{k}} n_{\boldsymbol{k}}!\right)^2 = N!\prod_{\boldsymbol{k}} n_{\boldsymbol{k}}!,$$

since there are $N!/\prod_{\boldsymbol{k}} n_{\boldsymbol{k}}!$ different distinguishable states in the symmetrized state, and each of these states occurs $\prod_{\boldsymbol{k}} n_{\boldsymbol{k}}!$ times. Therefore the correctly normalized Bose states are

$$|\{n_{\boldsymbol{k}}\}\rangle = \frac{1}{\sqrt{N!\prod_{\boldsymbol{k}} n_{\boldsymbol{k}}!}}\sum_{P\in S_N} P|\boldsymbol{k}_1, \dots \boldsymbol{k}_N\rangle.$$

The action of the operator $|\boldsymbol{k}'\rangle\langle\boldsymbol{k}|$ on this state is for $\boldsymbol{k} \neq \boldsymbol{k}'$

$$\begin{aligned}|\boldsymbol{k}'\rangle\langle\boldsymbol{k}|\dots, n_{\boldsymbol{k}}, \dots, n_{\boldsymbol{k}'}, \dots\rangle &= n_{\boldsymbol{k}}\sqrt{\frac{n_{\boldsymbol{k}'}+1}{n_{\boldsymbol{k}}}}|\dots, n_{\boldsymbol{k}}-1, \dots, n_{\boldsymbol{k}'}+1, \dots\rangle \\ &= \sqrt{n_{\boldsymbol{k}}(n_{\boldsymbol{k}'}+1)}|\dots, n_{\boldsymbol{k}}-1, \dots, n_{\boldsymbol{k}'}+1, \dots\rangle \\ &= a^+(\boldsymbol{k}')a(\boldsymbol{k})|\dots, n_{\boldsymbol{k}}, \dots, n_{\boldsymbol{k}'}, \dots\rangle,\end{aligned}$$

and for $\boldsymbol{k} = \boldsymbol{k}'$,

$$|\boldsymbol{k}\rangle\langle\boldsymbol{k}|\dots, n_{\boldsymbol{k}}, \dots\rangle = n_{\boldsymbol{k}}|\dots, n_{\boldsymbol{k}}, \dots\rangle = a^+(\boldsymbol{k})a(\boldsymbol{k})|\dots, n_{\boldsymbol{k}}, \dots\rangle.$$

i.e. we find that for 1-particle operators, the operator

$$K^{(1)} = \int d^3\boldsymbol{k}' \int d^3\boldsymbol{k}\, |\boldsymbol{k}'\rangle\langle\boldsymbol{k}'|K^{(1)}|\boldsymbol{k}\rangle\langle\boldsymbol{k}|$$

has the same effect in the first quantized theory as

$$K^{(2)} = \int d^3\boldsymbol{k}' \int d^3\boldsymbol{k}\, \langle\boldsymbol{k}'|K^{(1)}|\boldsymbol{k}\rangle a^+(\boldsymbol{k}')a(\boldsymbol{k})$$

has in the second quantized theory. E.g. the first quantized 1-particle Hamiltonian

$$H^{(1)} = \frac{\mathbf{p}^2}{2m} = \int d^3\boldsymbol{k}\,|\boldsymbol{k}\rangle \frac{\hbar^2\boldsymbol{k}^2}{2m}\langle\boldsymbol{k}|$$

becomes

$$H^{(2)} = \int d^3\boldsymbol{k}\,\frac{\hbar^2\boldsymbol{k}^2}{2m} a^+(\boldsymbol{k})a(\boldsymbol{k}).$$

Once the beasts $a^+(\boldsymbol{k})$ and $a(\boldsymbol{k})$ are let loose, it is easy to recognize from their commutation or anti-commutation relations that they create and annihilate particles, and the whole theory can be developed from there. The approach through quantization of Lagrangian field theories is preferred in this book because it also yields an elegant formalism for the identification of conservation laws and generalizes more naturally to the relativistic case.

17.9 Problems

17.1 Calculate the evolution equations $dN(t)/dt$ and $d\boldsymbol{P}(t)/dt$ for the number and momentum operators in the Heisenberg picture if the Hamiltonian is given by equation (17.2).

17.2 The relation $p_0 = -E/c$ in relativity motivates the identification of the Hamiltonian H with a timelike momentum operator $P_0 = -H/c$.
Show that the field operators in the Heisenberg picture satisfy the commutation relations

$$[P_\mu, \Psi(\boldsymbol{x}, t)] = \mathrm{i}\hbar\partial_\mu\Psi(\boldsymbol{x}, t).$$

17.3 Calculate the expectation value of the operator

$$\mathbf{x} = \int d^3\boldsymbol{x} \sum_\nu \psi_\nu^+(\boldsymbol{x})\boldsymbol{x}\psi_\nu(\boldsymbol{x})$$

for the two-particle state (17.48).

17.4 Calculate the expectation values $\langle H_0\rangle$ and $\langle V\rangle$ for kinetic and potential energy in the two-particle state (17.45) with identical particles.

17.5 Show that for pairs of spin-1 bosons, the interaction energy for states (17.48)

$$\langle V\rangle = \langle\Psi_{n,\sigma}(t), \Psi_{n',\sigma'}(t)|V|\Psi_{n,\sigma}(t), \Psi_{n',\sigma'}(t)\rangle = \frac{C_{nn'} + J_{nn'}\delta_{\sigma\sigma'}}{1 + \delta_{\sigma\sigma'}\delta_{nn'}}$$

corresponds to the following values for the interaction energy in the singlet, triplet, and quintuplet states,

$$E^{(0)}_{n,n'} = E^{(2)}_{n,n'} = \frac{C_{nn'} + J_{nn'}}{1 + \delta_{nn'}}, \quad E^{(1)}_{nn'} = \frac{C_{nn'} - J_{nn'}}{1 + \delta_{nn'}} = C_{nn'} - J_{nn'}.$$

Show also that these energies can be reproduced with an effective spin-spin interaction Hamiltonian

$$H_{n,n'} = \frac{1}{1+\delta_{nn'}}\left(C_{nn'} + \frac{1}{4}J_{nn'}\left(4 - 6(\boldsymbol{S}+\boldsymbol{S}')^2 + (\boldsymbol{S}+\boldsymbol{S}')^4\right)\right)$$
$$= \frac{1}{1+\delta_{nn'}}\left(C_{nn'} - J_{nn'} + J_{nn'}\boldsymbol{S}\cdot\boldsymbol{S}' + J_{nn'}(\boldsymbol{S}\cdot\boldsymbol{S}')^2\right). \tag{17.65}$$

17.6 Hartree-Fock equations

17.6a Calculate the expectation value of the Hamiltonian (17.53) for a three-particle state which is a tensor product of single particle factors for a helium nucleus and two electrons,

$$|\Phi\rangle = \int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\int d^3\boldsymbol{y}\,\psi^+_{e,\sigma}(\boldsymbol{x})\psi^+_{e,\sigma'}(\boldsymbol{x}')\psi^+_{\alpha,\nu}|0\rangle$$
$$\times\langle\boldsymbol{x}|\phi_n(t)\rangle\langle\boldsymbol{x}'|\phi_{n'}(t)\rangle\langle\boldsymbol{y}|\phi_N(t)\rangle.$$

Show that the requirement of minimal expectation value $\langle\Phi|H|\Phi\rangle$ under the constraints of normalized single particle wave functions yields a set of three non-linear coupled equations for the single particle wave functions. You have to use Lagrange multipliers to include the normalization constraints, i.e. you have to calculate the variational derivatives of the functional

$$F[\phi_n(t),\phi_{n'}(t),\phi_N(t)] = \langle\Phi|H|\Phi\rangle - \epsilon_n\left(\int d^3\boldsymbol{x}\,|\langle\boldsymbol{x}|\phi_n(t)\rangle|^2 - 1\right)$$
$$-\epsilon_{n'}\left(\int d^3\boldsymbol{x}\,|\langle\boldsymbol{x}|\phi_{n'}(t)\rangle|^2 - 1\right) - \epsilon_N\left(\int d^3\boldsymbol{x}\,|\langle\boldsymbol{x}|\phi_N(t)\rangle|^2 - 1\right),$$

e.g.

$$\frac{\delta}{\delta\phi_n(\boldsymbol{x})}F[\phi_n(t),\phi_{n'}(t),\phi_N(t)] = 0.$$

This yields intuitive versions of non-linearly coupled equations which look like time-independent Schrödinger equations. These equations are examples of *Hartree-Fock* equations[11]. The equations for the electrons contain exchange terms due to the presence of identical particles, and Hartree-Fock type equations have been successfully applied to calculate electronic configurations in atoms, molecules and solids. However, the limitation of the variation of the N particle states to tensor product states is a principal limitation of the Hartree-Fock method. The lowly hydrogen atom already told us that translation invariant interaction potentials $V(\boldsymbol{x}-\boldsymbol{x}')$ entangle two-particle states in such a way that the energy eigenstates of the coupled system cannot be written as tensor products of single particle states.

17.6b Show that the Lagrange multipliers ϵ_i add up to the sum of the kinetic

[11] Very good contemporary textbook discussions of Hartree-Fock equations can be found in [24,33,34], and a very comprehensive discussion of the uses of Hartree-Fock type equations in chemistry and condensed matter physics is contained in [10].

energy plus *twice* the potential energy of the system.

17.7 We consider field operators for spin-1/2 fermions,

$$\{\psi_\sigma(\boldsymbol{x}), \psi^+_{\sigma'}(\boldsymbol{x}')\} = \delta_{\sigma,\sigma'}\delta(\boldsymbol{x}-\boldsymbol{x}'),$$

$$\{\psi_\sigma(\boldsymbol{x}), \psi_{\sigma'}(\boldsymbol{x}')\} = 0, \quad \{\psi^+_\sigma(\boldsymbol{x}), \psi^+_{\sigma'}(\boldsymbol{x}')\} = 0.$$

17.7a The particle density operator is $n_\sigma(\boldsymbol{x}) = \psi^+_\sigma(\boldsymbol{x})\psi_\sigma(\boldsymbol{x})$. Show that the states $|\boldsymbol{x_1}, \sigma_1\rangle = \psi^+_{\sigma_1}(\boldsymbol{x_1})|0\rangle$ and $|\boldsymbol{x_1}, \sigma_1; \boldsymbol{x_2}, \sigma_2\rangle = \psi^+_{\sigma_1}(\boldsymbol{x_1})\psi^+_{\sigma_2}(\boldsymbol{x_2})|0\rangle$ are eigenstates of $n_\sigma(\boldsymbol{x})$ in the sense that relations of the kind

$$n_\sigma(\boldsymbol{x})|\boldsymbol{x_1}, \sigma_1\rangle = \lambda_{\sigma,\sigma_1}(\boldsymbol{x}, \boldsymbol{x_1})|\boldsymbol{x_1}, \sigma_1\rangle,$$

$$n_\sigma(\boldsymbol{x})|\boldsymbol{x_1}, \sigma_1; \boldsymbol{x_2}, \sigma_2\rangle = \lambda_{\sigma,\sigma_1,\sigma_2}(\boldsymbol{x}, \boldsymbol{x_1}, \boldsymbol{x_2})|\boldsymbol{x_1}, \sigma_1; \boldsymbol{x_2}, \sigma_2\rangle$$

hold. Calculate the "eigenvalues" $\lambda_{\sigma,\sigma_1}(\boldsymbol{x}, \boldsymbol{x_1})$ and $\lambda_{\sigma,\sigma_1,\sigma_2}(\boldsymbol{x}, \boldsymbol{x_1}, \boldsymbol{x_2})$.
17.7b We can define a density-density correlation operator

$$\mathcal{G}_{\sigma,\sigma'}(\boldsymbol{x}, \boldsymbol{x}') = n_\sigma(\boldsymbol{x})n_{\sigma'}(\boldsymbol{x}').$$

Evaluate the matrix elements $\langle \boldsymbol{x}_1, \sigma_1|\mathcal{G}_{\sigma,\sigma'}(\boldsymbol{x}, \boldsymbol{x}')|\boldsymbol{x_2}, \sigma_2\rangle$ of this operator in 1-particle states.

Solution

17.7a For the 1-particle state we can write

$$\begin{aligned} n_\sigma(\boldsymbol{x})|\boldsymbol{x_1}, \sigma_1\rangle &= \psi^+_\sigma(\boldsymbol{x})\{\psi_\sigma(\boldsymbol{x}), \psi^+_{\sigma_1}(\boldsymbol{x}_1)\}|0\rangle = \delta_{\sigma,\sigma_1}\delta(\boldsymbol{x}-\boldsymbol{x}_1)\psi^+_\sigma(\boldsymbol{x})|0\rangle \\ &= \delta_{\sigma,\sigma_1}\delta(\boldsymbol{x}-\boldsymbol{x}_1)|\boldsymbol{x_1}, \sigma_1\rangle. \end{aligned} \tag{17.66}$$

For the 2-particle state we use the relation $[A, BC] = \{A, B\}C - B\{A, C\}$ in

$$\begin{aligned} &n_\sigma(\boldsymbol{x})|\boldsymbol{x_1}, \sigma_1; \boldsymbol{x_2}, \sigma_2\rangle = \psi^+_\sigma(\boldsymbol{x})[\psi_\sigma(\boldsymbol{x}), \psi^+_{\sigma_1}(\boldsymbol{x}_1)\psi^+_{\sigma_2}(\boldsymbol{x}_2)]|0\rangle \\ &= \delta_{\sigma,\sigma_1}\delta(\boldsymbol{x}-\boldsymbol{x}_1)\psi^+_\sigma(\boldsymbol{x})\psi^+_{\sigma_2}(\boldsymbol{x}_2)|0\rangle - \delta_{\sigma,\sigma_2}\delta(\boldsymbol{x}-\boldsymbol{x}_2)\psi^+_\sigma(\boldsymbol{x})\psi^+_{\sigma_1}(\boldsymbol{x}_1)|0\rangle \\ &= (\delta_{\sigma,\sigma_1}\delta(\boldsymbol{x}-\boldsymbol{x}_1) + \delta_{\sigma,\sigma_2}\delta(\boldsymbol{x}-\boldsymbol{x}_2))\,|\boldsymbol{x_1}, \sigma_1; \boldsymbol{x_2}, \sigma_2\rangle. \end{aligned} \tag{17.67}$$

17.7b From the previous results and the orthogonality of the single-particle states (following from the anti-commutation relation between $\psi_{\sigma_1}(\boldsymbol{x}_1)$ and $\psi^+_{\sigma_2}(\boldsymbol{x}_2)$) we find

$$\begin{aligned} &\langle \boldsymbol{x}_1, \sigma_1|\mathcal{G}_{\sigma,\sigma'}(\boldsymbol{x}, \boldsymbol{x}')|\boldsymbol{x_2}, \sigma_2\rangle = \langle \boldsymbol{x}_1, \sigma_1|n_\sigma(\boldsymbol{x})n_{\sigma'}(\boldsymbol{x}')|\boldsymbol{x_2}, \sigma_2\rangle \\ &= \delta_{\sigma,\sigma_1}\delta(\boldsymbol{x}-\boldsymbol{x}_1)\delta_{\sigma',\sigma_2}\delta(\boldsymbol{x}'-\boldsymbol{x}_2)\delta_{\sigma_1,\sigma_2}\delta(\boldsymbol{x}_1-\boldsymbol{x}_2). \end{aligned}$$

17.8 Pair correlations in the Fermi gas

We know that the Pauli principle excludes two fermions from being in the same state, i.e. they cannot have the same quantum numbers. But what does that mean for continuous quantum numbers like the location $\boldsymbol{x}$ of a particle? What exactly does the statement mean: "Two electrons of equal spin cannot be in the same place"? How far apart do two electrons of equal spin have to

be to satisfy this constraint? We will figure this out in this problem.
In the previous problem we have found that the density-density correlation operator $\mathcal{G}_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') = n_\sigma(\boldsymbol{x})n_{\sigma'}(\boldsymbol{x}')$ has non-vanishing matrix elements for 1-particle states. Therefore we define the pair correlation operator

$$\begin{aligned}\hat{g}_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') &= \mathcal{G}_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') - \delta_{\sigma,\sigma'}\delta(\boldsymbol{x}-\boldsymbol{x}')n_\sigma(\boldsymbol{x}) \\ &= \psi^+_\sigma(\boldsymbol{x})\psi^+_{\sigma'}(\boldsymbol{x}')\psi_{\sigma'}(\boldsymbol{x}')\psi_\sigma(\boldsymbol{x})\end{aligned}$$

as a measure for the probability to find a fermion with spin orientation σ at the point $\boldsymbol{x}$, when we know that there is another fermion with spin orientation σ' at the point $\boldsymbol{x}'$. This ordering of operators eliminates the 1-particle matrix elements.
17.8a Show that the corresponding combination of classical electron densities divided by 2,

$$\frac{1}{2}\tilde{g}_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') = \frac{1}{2}n_\sigma(\boldsymbol{x})n_{\sigma'}(\boldsymbol{x}') - \frac{1}{2}\delta_{\sigma,\sigma'}\delta(\boldsymbol{x}-\boldsymbol{x}')n_\sigma(\boldsymbol{x}), \tag{17.68}$$

can be interpreted as a *probability density normalized to the number of fermion pairs* to find a fermion with spin projection $\hbar\sigma$ in $\boldsymbol{x}$ and a fermion with spin projection $\hbar\sigma'$ in $\boldsymbol{x}'$.
Hint: There are $N_\uparrow + N_\downarrow = N$ fermions in the volume V. What do you get from equation (17.68) by integrating over the volume?
17.8b The ground state of a free fermion gas is

$$|\Omega\rangle = \prod_{\boldsymbol{k},|\boldsymbol{k}|\le k_F} a^+_{1/2}(\boldsymbol{k})a^+_{-1/2}(\boldsymbol{k})|0\rangle,$$

where k_F is the Fermi wave number (12.17). Calculate the pair distribution function

$$g_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') = \langle\Omega|\hat{g}_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}')|\Omega\rangle$$

of the free fermion gas in the ground state.
Hints for the solution of 7b: With discrete momenta

$$\boldsymbol{k} = \frac{2\pi}{L}\boldsymbol{n}$$

the anti-commutation relation for fermionic creation and annihilation operators becomes

$$\{a_\sigma(\boldsymbol{k}), a^+_{\sigma'}(\boldsymbol{k}')\} = \delta_{\sigma,\sigma'}\delta_{\boldsymbol{k},\boldsymbol{k}'}.$$

The corresponding mode expansion for the annihilation operator in $\boldsymbol{x}$-space becomes

$$\psi_\sigma(\boldsymbol{x}) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{k}} a_\sigma(\boldsymbol{k})\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}),$$

and the inversion is

$$a_\sigma(\boldsymbol{k}) = \frac{1}{\sqrt{V}} \int_V d^3\boldsymbol{x}\, \psi_\sigma(\boldsymbol{x}) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}).$$

Substitute the mode expansions for ψ and ψ^+ into the operator $\hat{g}_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}')$. This yields a four-fold sum over momenta

$$\langle\Omega| \sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q},\boldsymbol{q}'} \ldots |\Omega\rangle.$$

In the next step, you can use that

$$a_\sigma(\boldsymbol{k})|\Omega\rangle = \Theta(k_F - k) a_\sigma(\boldsymbol{k})|\Omega\rangle, \quad \langle\Omega|a^+_\sigma(\boldsymbol{q}) = \Theta(k_F - q)\langle\Omega|a^+_\sigma(\boldsymbol{q}), \tag{17.69}$$

because e.g. in the first equation, if $k > k_F$, $a_\sigma(\boldsymbol{k})$ would simply anti-commute through all the creation operators in $|\Omega\rangle$ and yield zero through action on the vacuum $|0\rangle$. This reduces the four sums to sums over momenta inside the Fermi sphere,

$$\langle\Omega| \sum_{\{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q},\boldsymbol{q}'\}\le k_F} \ldots |\Omega\rangle.$$

For the following steps, we can use that for fermionic operators $(a^+_\sigma(\boldsymbol{k}))^2 = 0$ and therefore

$$k \le k_F: \quad a^+_\sigma(\boldsymbol{k})|\Omega\rangle = 0. \tag{17.70}$$

We can use this observation to replace operator products with commutators or anti-commutators, e.g.

$$q' \le k_F: \quad a^+_{\sigma'}(\boldsymbol{q}')a_{\sigma'}(\boldsymbol{k}')a_\sigma(\boldsymbol{k})|\Omega\rangle = [a^+_{\sigma'}(\boldsymbol{q}'), a_{\sigma'}(\boldsymbol{k}')a_\sigma(\boldsymbol{k})]|\Omega\rangle,$$

$$q \le k_F: \quad a^+_\sigma(\boldsymbol{q})a_{\sigma'}(\boldsymbol{k}')|\Omega\rangle = \{a^+_\sigma(\boldsymbol{q}), a_{\sigma'}(\boldsymbol{k}')\}|\Omega\rangle.$$

You can use these observations to get rid of all the operators in $g_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}')$. For the last steps, you have to figure out what the sum over all momenta inside a Fermi sphere is, $\sum_{\boldsymbol{k},|\boldsymbol{k}|\le k_F} 1$ (you know this sum because you know that there are N Fermions in the system). For another term, you have to use that for $N \gg 1$

$$\frac{1}{V} \sum_{\boldsymbol{k},|\boldsymbol{k}|\le k_F} f(\boldsymbol{k}) \simeq \frac{1}{(2\pi)^3} \int_{k\le k_F} d^3\boldsymbol{k}\, f(\boldsymbol{k}).$$

Solution

17.8a Integration of equation (17.68) over $\boldsymbol{x}$ and $\boldsymbol{x}'$ yields for identical spins e.g.

$$\frac{1}{2}\int d^3\boldsymbol{x} \int d^3\boldsymbol{x}'\, \tilde{g}_{\uparrow\uparrow}(\boldsymbol{x},\boldsymbol{x}') = \frac{1}{2} N_\uparrow(N_\uparrow - 1) = \mathcal{N}_{\uparrow\uparrow},$$

which is the number of independent fermion pairs with both fermions having spin up, and we also find

$$\frac{1}{2}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\tilde{g}_{\uparrow\downarrow}(\boldsymbol{x},\boldsymbol{x}') = \frac{1}{2}N_\uparrow N_\downarrow = \frac{1}{2}\mathcal{N}_{\uparrow\downarrow},$$

which is the number of independent fermion pairs with opposite spins if we take into account that we want e.g. spin up in the location $\boldsymbol{x}$ and spin down in $\boldsymbol{x}'$. Note also that summation over spin polarizations then yields

$$\begin{aligned}\sum_{\sigma,\sigma'}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\frac{1}{2}\tilde{g}_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') &= \frac{1}{2}N_\uparrow(N_\uparrow-1)+\frac{1}{2}N_\downarrow(N_\downarrow-1)+N_\uparrow N_\downarrow\\ &= \frac{1}{2}N(N-1) = \mathcal{N},\end{aligned}$$

i.e. the total number of independent fermions pairs.

17.8b The discussion below is a modification of the discussion given by Schwabl [34]. Other derivations of the exchange hole of the effective charge density experienced by a Hartree-Fock electron in a metal can be found in [10, 15]. We have

$$\begin{aligned}g_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') = \frac{1}{V^2}\sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q},\boldsymbol{q}'}&\exp\left[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}+\boldsymbol{k}'\cdot\boldsymbol{x}'-\boldsymbol{q}\cdot\boldsymbol{x}-\boldsymbol{q}'\cdot\boldsymbol{x}')\right]\\ &\times\langle\Omega|a^+_\sigma(\boldsymbol{q})a^+_{\sigma'}(\boldsymbol{q}')a_{\sigma'}(\boldsymbol{k}')a_\sigma(\boldsymbol{k})|\Omega\rangle.\end{aligned}$$

The observation (17.69) limits the sums over wave numbers,

$$\begin{aligned}g_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') = \frac{1}{V^2}\sum_{\{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q},\boldsymbol{q}'\}\le k_F}&\exp\left[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}+\boldsymbol{k}'\cdot\boldsymbol{x}'-\boldsymbol{q}\cdot\boldsymbol{x}-\boldsymbol{q}'\cdot\boldsymbol{x}')\right]\\ &\times\langle\Omega|a^+_\sigma(\boldsymbol{q})a^+_{\sigma'}(\boldsymbol{q}')a_{\sigma'}(\boldsymbol{k}')a_\sigma(\boldsymbol{k})|\Omega\rangle.\end{aligned}$$

For the next step we use (17.70), $\Theta(k_F-q')a^+_\sigma(\boldsymbol{q}')|\Omega\rangle = 0$, to replace operator products with commutators or anti-commutators:

$$\begin{aligned}g_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') &= \frac{1}{V^2}\sum_{\{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q},\boldsymbol{q}'\}\le k_F}\exp\left[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}+\boldsymbol{k}'\cdot\boldsymbol{x}'-\boldsymbol{q}\cdot\boldsymbol{x}-\boldsymbol{q}'\cdot\boldsymbol{x}')\right]\\ &\quad\times\langle\Omega|a^+_\sigma(\boldsymbol{q})[a^+_{\sigma'}(\boldsymbol{q}'),a_{\sigma'}(\boldsymbol{k}')a_\sigma(\boldsymbol{k})]|\Omega\rangle\\ &= \frac{1}{V^2}\sum_{\{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}\}\le k_F}\exp\left[\mathrm{i}(\boldsymbol{k}-\boldsymbol{q})\cdot\boldsymbol{x}\right]\langle\Omega|a^+_\sigma(\boldsymbol{q})a_\sigma(\boldsymbol{k})|\Omega\rangle\\ &\quad-\delta_{\sigma\sigma'}\frac{1}{V^2}\sum_{\{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{q}\}\le k_F}\exp\left[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}+\boldsymbol{k}'\cdot\boldsymbol{x}'-\boldsymbol{q}\cdot\boldsymbol{x}-\boldsymbol{k}\cdot\boldsymbol{x}')\right]\\ &\quad\times\langle\Omega|a^+_\sigma(\boldsymbol{q})a_{\sigma'}(\boldsymbol{k}')|\Omega\rangle\\ &= \frac{1}{V^2}\sum_{\{\boldsymbol{k},\boldsymbol{k}'\}\le k_F}1-\delta_{\sigma\sigma'}\frac{1}{V^2}\sum_{\{\boldsymbol{k},\boldsymbol{k}'\}\le k_F}\exp\left[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot(\boldsymbol{x}-\boldsymbol{x}')\right].\end{aligned}$$

Here the notation $\leq k_F$ under the summation indicates that e.g. the summation over $\boldsymbol{k}$ is over all vectors $\boldsymbol{k}$ inside the Fermi sphere: $|\boldsymbol{k}| \leq k_F$.
For the further evaluation we note that there are two fermions per momentum inside the Fermi sphere, and therefore

$$\frac{1}{V}\sum_{\boldsymbol{k},|\boldsymbol{k}|\leq k_F} 1 = \frac{N}{2V} = \frac{n}{2}.$$

This yields

$$\begin{aligned}
g_{\sigma,\sigma'}(\boldsymbol{x},\boldsymbol{x}') &= \frac{n^2}{4} - \delta_{\sigma\sigma'}\left|\frac{1}{V}\sum_{\boldsymbol{k},|\boldsymbol{k}|\leq k_F}\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]\right|^2 \\
&\approx \frac{n^2}{4} - \delta_{\sigma\sigma'}\left|\frac{1}{(2\pi)^3}\int_{k\leq k_F} d^3\boldsymbol{k}\,\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]\right|^2 \\
&= \frac{n^2}{4} - \delta_{\sigma\sigma'}\left|\frac{1}{(2\pi)^2}\int_0^{k_F} dk\int_{-1}^{1} d\xi\, k^2\exp[\mathrm{i}k|\boldsymbol{x}-\boldsymbol{x}'|\xi]\right|^2 \\
&= \frac{n^2}{4} - \delta_{\sigma\sigma'}\frac{1}{4\pi^4|\boldsymbol{x}-\boldsymbol{x}'|^2}\left|\int_0^{k_F} dk\, k\sin\left(k|\boldsymbol{x}-\boldsymbol{x}'|\right)\right|^2 \\
&= \frac{n^2}{4} - \delta_{\sigma\sigma'}\frac{\left[\sin\left(k_F|\boldsymbol{x}-\boldsymbol{x}'|\right) - k_F|\boldsymbol{x}-\boldsymbol{x}'|\cos\left(k_F|\boldsymbol{x}-\boldsymbol{x}'|\right)\right]^2}{4\pi^4|\boldsymbol{x}-\boldsymbol{x}'|^6}.
\end{aligned}$$

In particular, the result for equal spin orientation can be written as

$$\frac{4}{n^2}g_{\sigma,\sigma}(\boldsymbol{x},\boldsymbol{x}') = 1 - 9\frac{\left[\sin\left(k_F|\boldsymbol{x}-\boldsymbol{x}'|\right) - k_F|\boldsymbol{x}-\boldsymbol{x}'|\cos\left(k_F|\boldsymbol{x}-\boldsymbol{x}'|\right)\right]^2}{\left(k_F|\boldsymbol{x}-\boldsymbol{x}'|\right)^6},$$

where $n = k_F^3/3\pi^2$ was used. This means that up to a distance of order

$$\frac{\lambda_F}{2} = \frac{\pi}{k_F} = \left(\frac{\pi}{3n}\right)^{\frac{1}{3}}$$

the probability to find a fermion of like spin is significantly reduced: The Pauli principle prevents two fermions of like spin to be in the same place, even if there is no interaction between the fermions.
The function $\frac{4}{n^2}g_{\sigma,\sigma}(\boldsymbol{x},\boldsymbol{x}')$ is plotted for three ranges of the variable $x = k_F|\boldsymbol{x}-\boldsymbol{x}'|$ in Figures 17.1-17.3.
The first maximum $\frac{4}{n^2}g_{\sigma,\sigma}(\boldsymbol{x},\boldsymbol{x}') = 1$ is reached at

$$k_F|\boldsymbol{x}-\boldsymbol{x}'| \approx 4.4934,$$

i.e. depending on the maximal momentum in the fermion gas the minimal distance between two fermions of the *same* spin orientation is given by the minimal wavelength in the gas:

$$r_{hole} \approx 0.7\lambda_F. \tag{17.71}$$

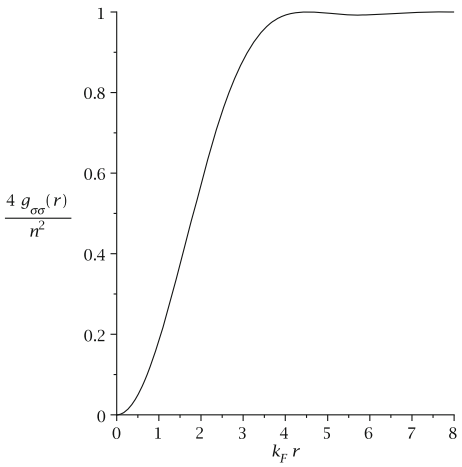


Figure 17.1: The scaled pair correlation function $4g_{\sigma,\sigma}(r)/n^2$ for $0 \leq k_F r \leq 8$.

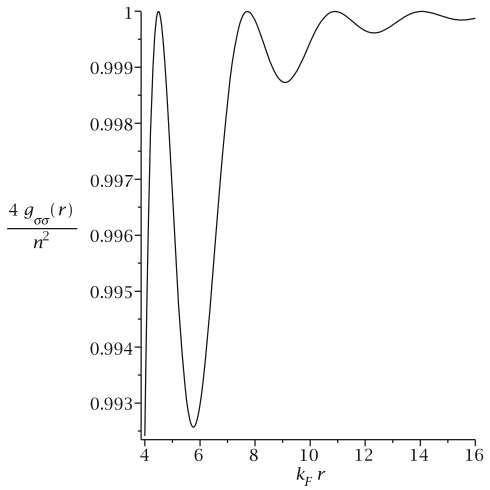


Figure 17.2: The scaled pair correlation function $4g_{\sigma,\sigma}(r)/n^2$ for $4 \leq k_F r \leq 16$.

On the other hand, the density of fermions with equal spin is $n/2$. Equal

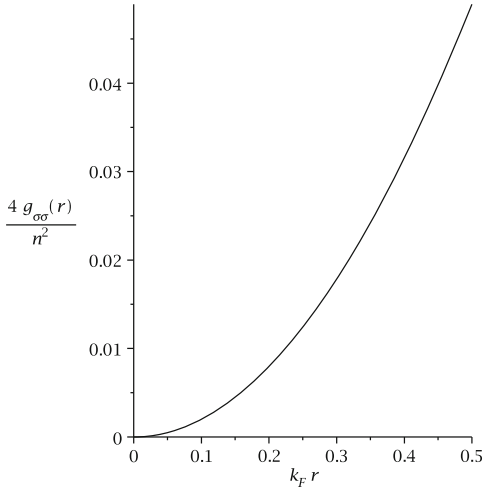


Figure 17.3: The scaled pair correlation function $4g_{\sigma,\sigma}(r)/n^2$ for $0 \leq k_F r \leq 0.5$.

separation between those fermions would correspond to a distance

$$a = \left(\frac{2}{n}\right)^{\frac{1}{3}},$$

and inserting the result for the Fermi momentum

$$k_F = \left(3\pi^2 n\right)^{\frac{1}{3}}, \quad \lambda_F = \left(\frac{8\pi}{3n}\right)^{\frac{1}{3}}$$

yields

$$a = \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} \lambda_F \simeq 0.62\lambda_F. \tag{17.72}$$

Comparison with r_{hole} (17.71) shows that the Pauli principle effectively repels fermions of equal spin such that they try to fill the available volume uniformly. Note that the existence of this *exchange hole* in the pair correlation between identical fermions of like spin has nothing to do e.g. with any electromagnetic interacion between the fermions. It is only a consequence of avoidance due to the Pauli principle. Stated differently (and presumably in the simplest possible way): The Pauli principle implies that free fermions of the same spin orientation try to occupy a volume as uniformly as possible to avoid contact.
If we want to add free fermions to a fermion gas of constant volume we have to increase the energy in the gas, thereby increasing the maximal momentum

in the gas, to squeeze more fermions into the volume and reduce the mean distance between fermions of like spin.
The presence of the exchange hole implies a local reduction of the charge density of the other electrons seen by an electron in a metal (a "Hartree-Fock electron in a jellium model" [10, 15, 23]),

$$\begin{aligned}\rho_e(r) &= -e\frac{n}{2} - e\frac{n}{2}\left(1 - \frac{9}{(k_F r)^6}\left[\sin(k_F r) - k_F r\cos(k_F r)\right]^2\right) \\ &= -en\left(1 - \frac{9}{2(k_F r)^6}\left[\sin(k_F r) - k_F r\cos(k_F r)\right]^2\right).\end{aligned}$$

This effective electron charge density is plotted in Figure 17.4.

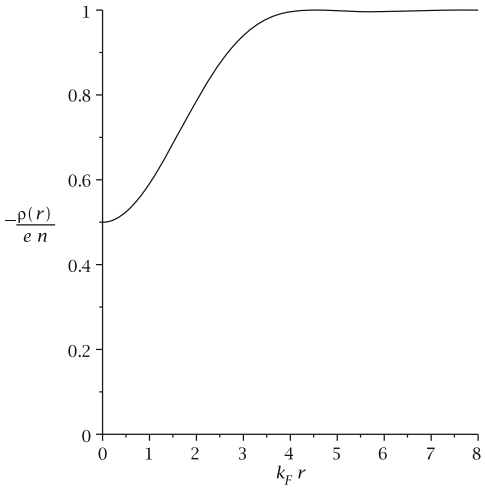


Figure 17.4: The effective scaled electron charge density $\rho_e(r)/(-en)$ in a metal is plotted for $0 \leq k_F r \leq 8$.

Chapter 18

Quantization of the Maxwell Field: Photons

We will now start to quantize the Maxwell field $A_\mu(x) = \{-\Phi(x)/c, \boldsymbol{A}(x)\}$ similar to the quantization of the Schrödinger field. The fact that electromagnetism has a gauge invariance implies that there are more components than actual dynamical degrees of freedom in the Maxwell field. This will make quantization a little more challenging than for the Schrödinger field, but we will overcome those difficulties.
The quantized Maxwell field also provides the first example of a relativistic quantum field theory.

18.1 Lagrange density and mode expansion for the Maxwell field

The equations of motion for the Maxwell field are the inhomogeneous Maxwell equations (recall that the homogeneous equations were solved through the introduction of the potentials A_μ),

$$\partial_\mu F^{\mu\nu} = \partial_\mu \left(\partial^\mu A^\nu - \partial^\nu A^\mu\right) = -\mu_0 j^\nu.$$

These equations can be written as

$$j^\nu + \frac{1}{\mu_0}\partial_\mu \left(\partial^\mu A^\nu - \partial^\nu A^\mu\right) = \frac{\partial \mathcal{L}}{\partial A_\nu} - \partial_\mu \frac{\partial \mathcal{L}}{\partial(\partial_\mu A_\nu)} = 0$$

if we use the Lagrange density

$$\mathcal{L} = j^\nu A_\nu - \frac{1}{4\mu_0} F_{\mu\nu}F^{\mu\nu} = \frac{\epsilon_0}{2}\boldsymbol{E}^2 - \frac{1}{2\mu_0}\boldsymbol{B}^2 + \boldsymbol{j}\cdot\boldsymbol{A} - \varrho\Phi. \tag{18.1}$$

This Lagrangian provides us with the canonically conjugate momentum for the vector potential $\boldsymbol{A}$:

$$\boldsymbol{\Pi}_{\boldsymbol{A}} = \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{A}}} = \epsilon_0(\dot{\boldsymbol{A}} + \boldsymbol{\nabla}\Phi) = -\epsilon_0 \boldsymbol{E},$$

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but

$$\Pi_\Phi = \frac{\partial \mathcal{L}}{\partial \dot{\Phi}} = 0$$

vanishes identically! Therefore we cannot simply impose canonical commutation relations between the four components A_μ of the 4-vector potential and four conjugate momenta Π_ν. To circumvent this problem we revisit Maxwell's equations,

$$\Delta\Phi + \boldsymbol{\nabla}\cdot\dot{\boldsymbol{A}} = -\frac{1}{\epsilon_0}\varrho, \tag{18.2}$$

$$\boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\boldsymbol{A}) - \Delta\boldsymbol{A} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{A} + \frac{1}{c^2}\frac{\partial}{\partial t}\boldsymbol{\nabla}\Phi = \mu_0\boldsymbol{j}. \tag{18.3}$$

One way to solve the problem with $\Pi_\Phi = 0$ is to eliminate $\boldsymbol{\nabla}\cdot\boldsymbol{A}$ from the equations of motion through the gauge freedom

$$\Phi(\boldsymbol{x},t) \to \Phi_f(\boldsymbol{x},t) = \Phi(\boldsymbol{x},t) - \dot{f}(\boldsymbol{x},t), \tag{18.4}$$

$$\boldsymbol{A}(\boldsymbol{x},t) \to \boldsymbol{A}_f(\boldsymbol{x},t) = \boldsymbol{A}(\boldsymbol{x},t) + \boldsymbol{\nabla}f(\boldsymbol{x},t), \tag{18.5}$$

i.e. we impose the gauge condition $\boldsymbol{\nabla}\cdot\boldsymbol{A}_f = 0$. The equation

$$\Delta f(\boldsymbol{x},t) = -\boldsymbol{\nabla}\cdot\boldsymbol{A}(\boldsymbol{x},t)$$

can be solved with the Green's function $G(r) = (4\pi r)^{-1}$ for the Laplace operator,

$$\Delta\frac{1}{4\pi|\boldsymbol{x}-\boldsymbol{x}'|} = -\delta(\boldsymbol{x}-\boldsymbol{x}'),$$

see equations (11.7) and (11.12) for $E = 0$,

$$f(\boldsymbol{x},t) = \frac{1}{4\pi}\int d^3\boldsymbol{x}'\,\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\boldsymbol{\nabla}\cdot\boldsymbol{A}(\boldsymbol{x}',t).$$

This gauge is denoted as *Coulomb gauge*.
We denote the gauge transformed fields again with Φ and $\boldsymbol{A}$, i.e. we have

$$\boldsymbol{\nabla}\cdot\boldsymbol{A}(\boldsymbol{x},t) = 0. \tag{18.6}$$

and

$$\Delta\Phi = -\frac{1}{\epsilon_0}\varrho, \tag{18.7}$$

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{A} - \Delta\boldsymbol{A} + \frac{1}{c^2}\frac{\partial}{\partial t}\boldsymbol{\nabla}\Phi = \mu_0\boldsymbol{j}. \tag{18.8}$$

We can now get rid of Φ by solving (18.7) again with the Green's function for the Laplace operator,

$$\Phi(\boldsymbol{x},t) = \frac{1}{4\pi\epsilon_0}\int d^3\boldsymbol{x}'\,\frac{\varrho(\boldsymbol{x}',t)}{|\boldsymbol{x}-\boldsymbol{x}'|}. \tag{18.9}$$

The resulting equation for $\boldsymbol{A}$ is

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta\right)\boldsymbol{A}(\boldsymbol{x},t) = \mu_0 \boldsymbol{j}(\boldsymbol{x},t) + \frac{\mu_0}{4\pi}\int d^3\boldsymbol{x}'\,\frac{\boldsymbol{x}-\boldsymbol{x}'}{|\boldsymbol{x}-\boldsymbol{x}'|^3}\frac{\partial}{\partial t}\varrho(\boldsymbol{x}',t)$$
$$= \mu_0 \boldsymbol{J}(\boldsymbol{x},t). \tag{18.10}$$

The new current $\boldsymbol{J}$ satisfies

$$\boldsymbol{\nabla}\cdot\boldsymbol{J}(\boldsymbol{x},t) = \boldsymbol{\nabla}\cdot\boldsymbol{j}(\boldsymbol{x},t) + \frac{\partial}{\partial t}\varrho(\boldsymbol{x},t) = 0 \tag{18.11}$$

due to charge conservation. We also require localization of charges and currents in the sense of

$$\lim_{|\boldsymbol{x}|\to\infty} |\boldsymbol{x}|\boldsymbol{J}(\boldsymbol{x},t) = 0. \tag{18.12}$$

Equation (18.10) can be solved e.g. with the retarded Green's function, cf. equation (I.50),

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta\right)G(\boldsymbol{x},t) = \delta(\boldsymbol{x})\delta(t), \quad G(\boldsymbol{x},t) = \frac{1}{4\pi r}\delta\Big(t-\frac{r}{c}\Big), \tag{18.13}$$

in the form

$$\boldsymbol{A}_J(\boldsymbol{x},t) = \mu_0\int d^3\boldsymbol{x}'\int dt'\,G(\boldsymbol{x}-\boldsymbol{x}',t-t')\boldsymbol{J}(\boldsymbol{x}',t')$$
$$= \frac{\mu_0}{4\pi}\int d^3\boldsymbol{x}'\,\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\boldsymbol{J}\left(\boldsymbol{x}',t-\frac{|\boldsymbol{x}-\boldsymbol{x}'|}{c}\right). \tag{18.14}$$

This satisfies $\boldsymbol{\nabla}\cdot\boldsymbol{A}_J(\boldsymbol{x},t) = 0$ due to (18.11,18.12).
The vector field is only a special solution of the inhomogeneous equation (18.10), and the general solution will be a superposition

$$\boldsymbol{A}(\boldsymbol{x},t) = \boldsymbol{A}_J(\boldsymbol{x},t) + \boldsymbol{A}_D(\boldsymbol{x},t)$$

of the special inhomogeneous solution with the general solution of the homogeneous equations

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \Delta\right)\boldsymbol{A}_D(\boldsymbol{x},t) = 0. \tag{18.15}$$

The homogeneous solution still has to satisfy the gauge condition $\boldsymbol{\nabla}\cdot\boldsymbol{A}_D = 0$, because the total vector potential $\boldsymbol{A}$ has to satisfy this condition.
Fourier decomposition

$$\boldsymbol{A}_D(\boldsymbol{x},t) = \frac{1}{4\pi^2}\int d^3\boldsymbol{k}\int d\omega\,\boldsymbol{A}_D(\boldsymbol{k},\omega)\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)]\,, \tag{18.16}$$

$$\boldsymbol{A}_D(\boldsymbol{k},\omega) = \frac{1}{4\pi^2}\int d^3\boldsymbol{x}\int dt\,\boldsymbol{A}_D(\boldsymbol{x},t)\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega t)]$$

transforms the condition $\boldsymbol{\nabla}\cdot\boldsymbol{A}_D(\boldsymbol{x},t)=0$ and the equation (18.15) into

$$\boldsymbol{k}\cdot\boldsymbol{A}_D(\boldsymbol{k},\omega)=0 \tag{18.17}$$

and

$$\left(\boldsymbol{k}^2-\frac{\omega^2}{c^2}\right)\boldsymbol{A}_D(\boldsymbol{k},\omega)=0. \tag{18.18}$$

Equation (18.17) is the statement that photons are transverse, whereas equation (18.18) implies that $\boldsymbol{A}_D(\boldsymbol{k},\omega)$ can be written as

$$\boldsymbol{A}_D(\boldsymbol{k},\omega)=\sqrt{\frac{\pi\hbar\mu_0 c}{k}}\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\left(a_\alpha(\boldsymbol{k})\delta(\omega-ck)+a_\alpha^+(-\boldsymbol{k})\delta(\omega+ck)\right), \tag{18.19}$$

where the prefactor so far is a matter of convention and the two vectors $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ are a Cartesian basis in the plane orthogonal to $\boldsymbol{k}$:

$$\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\boldsymbol{\epsilon}_\beta(\boldsymbol{k})=\delta_{\alpha\beta},\quad \boldsymbol{k}\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})=0.$$

Inserting (18.19) into (18.16) yields

$$\begin{aligned}\boldsymbol{A}_D(\boldsymbol{x},t)=\sqrt{\frac{\hbar\mu_0 c}{(2\pi)^3}}\int\frac{d^3\boldsymbol{k}}{\sqrt{2k}}\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(&a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\\&+a_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big),\end{aligned} \tag{18.20}$$

and for the fields

$$\begin{aligned}\boldsymbol{E}_D(\boldsymbol{x},t)&=-\frac{\partial}{\partial t}\boldsymbol{A}_D(\boldsymbol{x},t)\\&=\mathrm{i}\sqrt{\frac{\hbar\mu_0 c^3}{(2\pi)^3}}\int d^3\boldsymbol{k}\,\sqrt{\frac{k}{2}}\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\\&\quad-a_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big),\end{aligned} \tag{18.21}$$

$$\begin{aligned}\boldsymbol{B}_D(\boldsymbol{x},t)&=\boldsymbol{\nabla}\times\boldsymbol{A}_D(\boldsymbol{x},t)\\&=\mathrm{i}\sqrt{\frac{\hbar\mu_0 c}{(2\pi)^3}}\int\frac{d^3\boldsymbol{k}}{\sqrt{2k}}\sum_{\alpha=1}^{2}\boldsymbol{k}\times\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\\&\quad-a_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big).\end{aligned} \tag{18.22}$$

Inversion of equations (18.20,18.21) yields

$$\begin{aligned}a_\alpha(\boldsymbol{k})=\int\frac{d^3\boldsymbol{x}}{\sqrt{(2\pi)^3 2\mu_0\hbar c}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\left(\sqrt{k}\boldsymbol{A}_D(\boldsymbol{x},t)+\frac{\mathrm{i}}{c\sqrt{k}}\dot{\boldsymbol{A}}_D(\boldsymbol{x},t)\right)\\\times\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)],\end{aligned}$$

$$a_\alpha^+(\boldsymbol{k}) = \int \frac{d^3\boldsymbol{x}}{\sqrt{(2\pi)^3 2\mu_0\hbar c}} \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \cdot \left(\sqrt{k}\boldsymbol{A}_D(\boldsymbol{x},t) - \frac{\mathrm{i}}{c\sqrt{k}}\dot{\boldsymbol{A}}_D(\boldsymbol{x},t) \right) \times \exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - ckt)].$$

We can think of the vector potential (18.20) as a state $|A_D(t)\rangle$ with components

$$\langle \boldsymbol{k},\alpha|A_D(t)\rangle = \sqrt{\frac{\hbar\mu_0 c}{2k}} \left(a_\alpha(\boldsymbol{k})\exp(-\mathrm{i}ckt) + a_\alpha^+(-\boldsymbol{k})\exp(\mathrm{i}ckt) \right) \tag{18.23}$$

in wave vector space, and

$$\langle \boldsymbol{x},i|A_D(t)\rangle = \sqrt{\frac{\hbar\mu_0 c}{(2\pi)^3}} \int \frac{d^3\boldsymbol{k}}{\sqrt{2k}} \sum_{\alpha=1}^{2} \epsilon_\alpha^i(\boldsymbol{k}) \Big(a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - ckt)] + a_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - ckt)] \Big) \tag{18.24}$$

in $\boldsymbol{x}$ space. This corresponds to transformation matrices

$$\langle \boldsymbol{x},i|\boldsymbol{k},\alpha\rangle = \frac{1}{\sqrt{2\pi}^3}\epsilon_\alpha^i(\boldsymbol{k})\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}),$$

and we can easily check the completeness relations

$$\begin{aligned}\langle \boldsymbol{k},\alpha|\boldsymbol{k}',\beta\rangle &= \int d^3\boldsymbol{x} \sum_i \langle \boldsymbol{k},\alpha|\boldsymbol{x},i\rangle\langle \boldsymbol{x},i|\boldsymbol{k}',\beta\rangle = \delta(\boldsymbol{k}-\boldsymbol{k}')\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\boldsymbol{\epsilon}_\beta(\boldsymbol{k}) \\ &= \delta(\boldsymbol{k}-\boldsymbol{k}')\delta_{\alpha\beta},\end{aligned} \tag{18.25}$$

$$\begin{aligned}\langle \boldsymbol{x},i|\boldsymbol{x}',j\rangle &= \int d^3\boldsymbol{k} \sum_\alpha \langle \boldsymbol{x},i|\boldsymbol{k},\alpha\rangle\langle \boldsymbol{k},\alpha|\boldsymbol{x}',j\rangle \\ &= \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]\sum_\alpha \epsilon_\alpha^i(\boldsymbol{k})\epsilon_\alpha^j(\boldsymbol{k}) \\ &= \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\ \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]P_\perp^{ij}(\boldsymbol{k}) \\ &= \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\ \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]\left(\delta^{ij} - \frac{k^i k^j}{k^2}\right) \\ &= \delta_\perp^{ij}(\boldsymbol{x}-\boldsymbol{x}').\end{aligned} \tag{18.26}$$

Here the equation

$$\sum_{\alpha=1}^{2} \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \otimes \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) = \underline{\mathbf{1}} - \hat{\boldsymbol{k}} \otimes \hat{\boldsymbol{k}}$$

has been used, cf. the decomposition of the identity (4.11). Equation (18.26) defines the *transverse δ function*.

Energy-momentum tensor for the free Maxwell field

The Lagrange density for the free Maxwell field,

$$\mathcal{L}_D = -\frac{1}{4\mu_0} F_{D,\mu\nu} F_D^{\mu\nu},$$

yields a canonical energy-momentum tensor

$$\Theta_\mu{}^\nu = \eta_\mu{}^\nu \mathcal{L}_D - \partial_\mu A_{D,\lambda} \frac{\partial \mathcal{L}_D}{\partial(\partial_\nu A_{D,\lambda})} = \frac{1}{\mu_0}\left(\partial_\mu A_{D,\lambda} F_D^{\nu\lambda} - \frac{1}{4}\eta_\mu{}^\nu F_{D,\kappa\lambda} F_D^{\kappa\lambda}\right)$$

which is not gauge invariant. However, the free equation $\partial_\nu F_D^{\nu\lambda} = 0$ implies a trivial conservation law

$$-\frac{1}{\mu_0}\partial_\nu\left(\partial_\lambda A_{D,\mu} F_D^{\nu\lambda}\right) = 0$$

which can be added to the conservation law for the free fields, $\partial_\nu \Theta_\mu{}^\nu = 0$. In this way we can improve the energy-momentum tensor $\Theta_\mu{}^\nu$ to a gauge invariant energy-momentum tensor

$$T_\mu{}^\nu = \Theta_\mu{}^\nu - \frac{1}{\mu_0}\partial_\lambda A_{D,\mu} F_D^{\nu\lambda} = \frac{1}{\mu_0}\left(F_{D,\mu\lambda} F_D^{\nu\lambda} - \frac{1}{4}\eta_\mu{}^\nu F_{D,\kappa\lambda} F_D^{\kappa\lambda}\right).$$

The corresponding energy-momentum density vector

$$\mathcal{P}_\mu = \frac{1}{c} T_\mu{}^0$$

yields the well known expressions for the energy and momentum densities of electromagnetic fields,

$$\mathcal{H} = -c\mathcal{P}_0 = -T_0{}^0 = \frac{\epsilon_0}{2}\boldsymbol{E}_D^2 + \frac{1}{2\mu_0}\boldsymbol{B}_D^2, \tag{18.27}$$

$$\boldsymbol{\mathcal{P}} = \epsilon_0 \boldsymbol{E}_D \times \boldsymbol{B}_D. \tag{18.28}$$

The components of the energy current density (the Poynting vector) are given by the components $-cT_0{}^i$ (because $-\partial_t T_0{}^0 = -c\partial_0 T_0{}^0 = c\partial_i T_0{}^i$):

$$\boldsymbol{\mathcal{S}} = \frac{1}{\mu_0}\boldsymbol{E}_D \times \boldsymbol{B}_D = c^2 \boldsymbol{\mathcal{P}}. \tag{18.29}$$

We are interested in the energy and momentum densities for the free fields $\boldsymbol{A}_D(\boldsymbol{x}, t)$, because those will become the freely evolving field operators in the Dirac picture.

18.2 Photons

In the previous section we got rid of Φ and even of the longitudinal component of $\boldsymbol{A}$. Now we might be tempted to impose canonical commutation relations $[A_i(\boldsymbol{x},t),\Pi_j(\boldsymbol{x}',t)] \sim \mathrm{i}\hbar\delta_{ij}\delta(\boldsymbol{x}-\boldsymbol{x}')$. However, this would be inconsistent, since equation (18.6) implies that application of $\partial/\partial x_i$ and summation over i on the left hand side would yield zero, but on the right hand side would not yield zero! This problem arises irrespective of whether we wish to quantize the full vector potential $\boldsymbol{A}$ or only the free vector potential $\boldsymbol{A}_D$. Therefore we have to invoke the transverse δ-function (18.26) to formulate the canonical commutation relations for the Maxwell field. We will use these relations primarily for the Dirac picture operators,

$$\begin{aligned}[A_{D,i}(\boldsymbol{x},t),\dot{A}_{D,j}(\boldsymbol{x}',t)] &= \frac{\mathrm{i}\hbar}{\epsilon_0(2\pi)^3}\int d^3\boldsymbol{k}\left(\delta_{ij}-\frac{k_ik_j}{\boldsymbol{k}^2}\right)\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]\\ &= \frac{\mathrm{i}\hbar}{\epsilon_0(2\pi)^3}\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}\epsilon_{\alpha,i}(\boldsymbol{k})\epsilon_{\alpha,j}(\boldsymbol{k})\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')],\end{aligned}$$

or in short form

$$[A_{D,i}(\boldsymbol{x},t),\dot{A}_{D,j}(\boldsymbol{x}',t)] = \frac{\mathrm{i}\hbar}{\epsilon_0}\delta^{\perp}_{ij}(\boldsymbol{x}-\boldsymbol{x}'). \tag{18.30}$$

The remaining relations are

$$[A_{D,i}(\boldsymbol{x},t),A_{D,j}(\boldsymbol{x}',t)] = 0, \quad [\dot{A}_{D,i}(\boldsymbol{x},t),\dot{A}_{D,j}(\boldsymbol{x}',t)] = 0. \tag{18.31}$$

The relations (18.30,18.31) yield for the operators $a_\alpha(\boldsymbol{k})$, $a^+_\beta(\boldsymbol{k}')$ harmonic oscillator relations,

$$[a_\alpha(\boldsymbol{k}),a_\beta(\boldsymbol{k}')] = 0, \quad [a^+_\alpha(\boldsymbol{k}),a^+_\beta(\boldsymbol{k}')] = 0, \quad [a_\alpha(\boldsymbol{k}),a^+_\beta(\boldsymbol{k}')] = \delta_{\alpha\beta}\delta(\boldsymbol{k}-\boldsymbol{k}').$$

The prefactor in (18.19) was chosen such that no extra factor appears in the commutation relation of $a_\alpha(\boldsymbol{k})$ and $a^+_\beta(\boldsymbol{k}')$.
The energy and momentum densities (18.27) and (18.28) yield energy and momentum operators

$$\begin{aligned}H &= \int d^3\boldsymbol{x}\left(\frac{\epsilon_0}{2}\boldsymbol{E}_D^2+\frac{1}{2\mu_0}\boldsymbol{B}_D^2\right) = \sum_\alpha\int d^3\boldsymbol{k}\,\hbar ck\,a^+_\alpha(\boldsymbol{k})a_\alpha(\boldsymbol{k}),\\ \boldsymbol{P} &= \epsilon_0\int d^3\boldsymbol{x}\,\boldsymbol{E}_D\times\boldsymbol{B}_D = \sum_\alpha\int d^3\boldsymbol{k}\,\hbar\boldsymbol{k}\,a^+_\alpha(\boldsymbol{k})a_\alpha(\boldsymbol{k}).\end{aligned}$$

From these expressions we can infer by the meanwhile standard methods that $a^+_\alpha(\boldsymbol{k})$ creates a photon of momentum $\hbar\boldsymbol{k}$, energy $\hbar ck$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$, while $a_\alpha(\boldsymbol{k})$ annihilates such a photon. In particular,

$$|\boldsymbol{k},\alpha\rangle = a^+_\alpha(\boldsymbol{k})|0\rangle$$

is a single photon state with momentum $\hbar\boldsymbol{k}$, energy $\hbar ck$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$.

If we want to construct a creation operator $a^+_\alpha(\boldsymbol{x})$ in $\boldsymbol{x}$ space (corresponding to the operator $\psi^+(\boldsymbol{x})$ in Schrödinger theory) we find

$$\begin{aligned} a^+_\alpha(\boldsymbol{x}) &= \frac{1}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\, a^+_\alpha(\boldsymbol{k})\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \\ &= \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\int d^3\boldsymbol{x}'\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\left(\sqrt{\frac{k}{2\mu_0 c\hbar}}\boldsymbol{A}_D(\boldsymbol{x}',t)\right. \\ &\quad \left. -\frac{\mathrm{i}}{\sqrt{2k\mu_0 c^3\hbar}}\dot{\boldsymbol{A}}_D(\boldsymbol{x}',t)\right)\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}'-\boldsymbol{x})-\mathrm{i}ckt]. \end{aligned}$$

The expression on the right hand side is time-independent and can just as well be written in terms of the Schrödinger picture operators $\boldsymbol{A}(\boldsymbol{x}) = \boldsymbol{A}_D(\boldsymbol{x},0)$ and $\dot{\boldsymbol{A}}(\boldsymbol{x}) = \dot{\boldsymbol{A}}_D(\boldsymbol{x},0)$. However, the important observation is that contrary to Schrödinger theory, the original operator in $\boldsymbol{x}$ space, $\boldsymbol{A}(\boldsymbol{x},t)$, is not a pure annihilation or creation operator any more, but instead is a superposition of annihilation and creation operators. This is a generic feature of relativistic field operators. The property $a^+(\boldsymbol{x}) = \psi^+(\boldsymbol{x})$ is a special feature of the non-relativistic Schrödinger field.

The time evolution of the free photon operators in $\boldsymbol{k}$ space is given by the standard Heisenberg evolution equations,

$$a_{D\alpha}(\boldsymbol{k},t) = a_\alpha(\boldsymbol{k})\exp(-\mathrm{i}ckt) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)a_\alpha(\boldsymbol{k})\exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right),$$

$$\frac{\partial}{\partial t}a_{D\alpha}(\boldsymbol{k},t) = \frac{\mathrm{i}}{\hbar}[H, a_{D\alpha}(\boldsymbol{k},t)],$$

and therefore we also have for the field operators in $\boldsymbol{x}$ space

$$\boldsymbol{A}_D(\boldsymbol{x},t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)\boldsymbol{A}_D(\boldsymbol{x})\exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right),$$

but to recover the evolution equation (18.15) in $\boldsymbol{x}$ space we have to use iterated Heisenberg evolution equations,

$$\frac{\partial}{\partial t}\boldsymbol{A}_D(\boldsymbol{x},t) = \frac{\mathrm{i}}{\hbar}[H, \boldsymbol{A}_D(\boldsymbol{x},t)] = -\boldsymbol{E}_D(\boldsymbol{x},t),$$

$$\frac{\partial^2}{\partial t^2}\boldsymbol{A}_D(\boldsymbol{x},t) = -\frac{\mathrm{i}}{\hbar}[H, \boldsymbol{E}_D(\boldsymbol{x},t)] = -\frac{1}{\hbar^2}[H,[H, \boldsymbol{A}_D(\boldsymbol{x},t)]].$$

This is a general property of bosonic relativistic fields.

18.3 Coherent states of the electromagnetic field

We can directly apply what we have learned about coherent oscillator states to construct a quantum state with the property that the operator $\boldsymbol{E}_D(\boldsymbol{x},t)$ (18.21) yields a classical electromagnetic wave as expectation value,

$$\begin{aligned}\langle\boldsymbol{\mathcal{E}}|\boldsymbol{E}_D(\boldsymbol{x},t)|\boldsymbol{\mathcal{E}}\rangle &= \boldsymbol{\mathcal{E}}(\boldsymbol{x},t)\\ &= \mathrm{i}\sqrt{\frac{\hbar\mu_0 c^3}{(2\pi)^3}}\int d^3\boldsymbol{k}\,\sqrt{\frac{k}{2}}\sum_{\alpha=1}^{2}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(\zeta_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\\ &\quad -\zeta_\alpha^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt)]\Big).\end{aligned}\tag{18.32}$$

The results of Section 6.5 imply that the state $|\boldsymbol{\mathcal{E}}\rangle$ can be unitarily generated out of the vacuum[1],

$$|\boldsymbol{\mathcal{E}}\rangle = \exp\left(\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}\left(\zeta_\alpha(\boldsymbol{k})a_\alpha^+(\boldsymbol{k})-\zeta_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k})\right)\right)|0\rangle.$$

The corresponding equations in the Schrödinger picture are

$$\begin{aligned}&\langle\boldsymbol{\mathcal{E}}(t)|\boldsymbol{E}(\boldsymbol{x})|\boldsymbol{\mathcal{E}}(t)\rangle = \boldsymbol{\mathcal{E}}(\boldsymbol{x},t),\\ &|\boldsymbol{\mathcal{E}}(t)\rangle = \exp\left(\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}\left(\zeta_\alpha(\boldsymbol{k},t)a_\alpha^+(\boldsymbol{k})-\zeta_\alpha^+(\boldsymbol{k},t)a_\alpha(\boldsymbol{k})\right)\right)|0\rangle,\end{aligned}\tag{18.33}$$

with

$$\zeta_\alpha(\boldsymbol{k},t) = \zeta_\alpha(\boldsymbol{k})\exp(-\mathrm{i}ckt).$$

The average photon number in the electromagnetic wave is

$$\langle n\rangle = \langle\boldsymbol{\mathcal{E}}|\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}a_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k})|\boldsymbol{\mathcal{E}}\rangle = \int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}|\zeta_\alpha(\boldsymbol{k})|^2$$

and we find with

$$\begin{aligned}\left(\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}a_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k})\right)^2 &= \int d^3\boldsymbol{k}\int d^3\boldsymbol{k}'\sum_{\alpha,\alpha'=1}^{2}a_\alpha^+(\boldsymbol{k})a_{\alpha'}^+(\boldsymbol{k}')a_{\alpha'}(\boldsymbol{k}')a_\alpha(\boldsymbol{k})\\ &\quad +\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}a_\alpha^+(\boldsymbol{k})a_\alpha(\boldsymbol{k})\end{aligned}$$

the relations

$$\langle n^2\rangle = \left(\int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}|\zeta_\alpha(\boldsymbol{k})|^2\right)^2 + \int d^3\boldsymbol{k}\sum_{\alpha=1}^{2}|\zeta_\alpha(\boldsymbol{k})|^2,$$

[1] R.J. Glauber, Phys. Rev. 131, 2766 (1963).

$$\Delta n = \sqrt{\langle n \rangle} = \left(\int d^3\boldsymbol{k} \sum_{\alpha=1}^{2} |\zeta_\alpha(\boldsymbol{k})|^2 \right)^{1/2}, \quad \frac{\Delta n}{\langle n \rangle} = \frac{1}{\sqrt{\langle n \rangle}}.$$

Every free quantum field has an expansion in terms of oscillator operators, and therefore each quantum field has coherent states which yield classical expectation values for the field. They are particularly important for electromagnetic fields because classical electromagnetic waves are so abundant, readily available, and of technical relevance. This is a consequence of boson statistics and of the vanishing mass and charge of photons. Generating and packing together huge numbers of photons is very inexpensive in terms of energy.

18.4 Photon coupling to relative motion

The discussion of photon interactions with atoms or molecules usually does not involve discussions of photon interactions with the individual constituent electrons and nuclei, but implicitly assumes an effective coupling to the quasi-particles which describe the relative motion between nuclei and electrons. However, this procedure is not straightforward to justify and it is instructive to revisit the problem of separation of center of mass motion and relative motion in the presence of electromagnetic fields.
The two-particle Hamiltonian (7.1) with electromagnetic potentials takes the form

$$H = \frac{1}{2m_1} \left(\mathbf{p}_1 - q_1 \boldsymbol{A}(\mathbf{x}_1, t) \right)^2 + \frac{1}{2m_2} \left(\mathbf{p}_2 - q_2 \boldsymbol{A}(\mathbf{x}_2, t) \right)^2 + V(|\mathbf{x}_1 - \mathbf{x}_2|).$$

Substitution of the single particle momenta with the total momentum and the effective momentum in the relative motion (7.6) yields

$$\begin{aligned} H = & \frac{1}{2M} \left(\mathbf{P} - q_1 \boldsymbol{A}(\mathbf{x}_1, t) - q_2 \boldsymbol{A}(\mathbf{x}_2, t) \right)^2 \\ & + \frac{1}{2\mu} \left(\mathbf{p} - \frac{m_2 q_1 \boldsymbol{A}(\mathbf{x}_1, t) - m_1 q_2 \boldsymbol{A}(\mathbf{x}_2, t)}{M} \right)^2 + V(|\mathbf{x}_1 - \mathbf{x}_2|). \end{aligned} \tag{18.34}$$

Now we assume that the electromagnetic potentials vary weakly over the extension of the two-particle system,

$$\boldsymbol{A}(\boldsymbol{x}_1, t) \simeq \boldsymbol{A}(\boldsymbol{x}_2, t) \simeq \boldsymbol{A}(\boldsymbol{R}, t). \tag{18.35}$$

This yields an effective Hamiltonian

$$H = \frac{1}{2M} \left(\mathbf{P} - Q \boldsymbol{A}(\mathbf{R}, t) \right)^2 + \frac{1}{2\mu} \left(\mathbf{p} - q \boldsymbol{A}(\mathbf{R}, t) \right)^2 + V(|\mathbf{r}|), \tag{18.36}$$

with a total charge $Q = q_1 + q_2$ for the center of mass motion, and a reduced charge of the quasi-particle describing relative motion,

$$q = \frac{m_2 q_1 - m_1 q_2}{m_1 + m_2}. \tag{18.37}$$

Even the simplifying assumption (18.35) does not allow for separation of the center of mass motion any more, but we also assume that the photon terms can be treated as perturbations of the two-particle system. In this case we are left with an effective single-particle Hamiltonian for the relative motion in the center of mass frame

$$H = \frac{1}{2\mu}\left(\mathbf{p} - q\boldsymbol{A}(t)\right)^2 + V(|\mathbf{r}|). \tag{18.38}$$

Equation (18.37) for the effective charge q yields $q = q_1$ if $q_2 = -q_1$, and $m_2 \gg m_1$ also implies $q \simeq q_1$. This entails that in atoms or molecules, we can think of photons as effectively coupling to the electrons if the photon wavelengths hc/E_γ are large compared to the size of the atoms or molecules. Please also note that the derivation of (18.38) required negligible spatial variation of the photon terms over the extension of the unperturbed wave functions for relative motion, to justify minimal photon coupling into the Hamiltonian for relative motion. Dipole approximation and electromagnetic coupling to the Hamiltonian for relative motion therefore use the same premise.

18.5 Photon emission rates

The calculation of transition probabilities between Fock states requires time-dependent perturbation theory in the second quantized formalism.
The Hamiltonian for a coupled system of non-relativistic charged particles and photons is

$$\begin{aligned} H &= H_0 + H_I + H_{II} \\ &= \int d^3\boldsymbol{x} \left(\frac{\hbar^2}{2m} \sum_\sigma (\boldsymbol{\nabla}\psi_\sigma^+)\cdot\boldsymbol{\nabla}\psi_\sigma + \sum_\sigma \psi_\sigma^+ V \psi_\sigma + \frac{\epsilon_0}{2}\dot{\boldsymbol{A}}^2 + \frac{1}{2\mu_0}(\boldsymbol{\nabla}\times\boldsymbol{A})^2 \right. \\ &\quad \left. + \mathrm{i}\frac{q\hbar}{2m}\boldsymbol{A}\cdot\sum_\sigma \left(\psi_\sigma^+ \overleftrightarrow{\boldsymbol{\nabla}}\, \psi_\sigma\right) + \frac{q^2}{2m}\sum_\sigma \psi_\sigma^+ \boldsymbol{A}^2 \psi_\sigma \right), \end{aligned} \tag{18.39}$$

where V is an intra-atomic or intra-molecular potential and the interaction terms between the charged particles and the photons are

$$H_I = \int d^3\boldsymbol{x} \sum_\sigma \mathrm{i}\frac{q\hbar}{2m}\boldsymbol{A}\cdot\left(\psi_\sigma^+ \overleftrightarrow{\boldsymbol{\nabla}}\, \psi_\sigma\right), \quad H_{II} = \int d^3\boldsymbol{x}\, \frac{q^2}{2m}\sum_\sigma \psi_\sigma^+ \boldsymbol{A}^2 \psi_\sigma.$$

In principle there is also a term

$$H_C = \frac{q^2}{8\pi\epsilon_0}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}' \sum_{\sigma,\sigma'} \psi_\sigma^+(\boldsymbol{x})\psi_{\sigma'}^+(\boldsymbol{x}')\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\psi_{\sigma'}(\boldsymbol{x}')\psi_\sigma(\boldsymbol{x})$$

from substitution of the scalar potential in Coulomb gauge. However, we will only study transitions with single matter particles in the initial state, where H_C will not contribute.

For the following calculations we use hydrogen states as an example to illustrate the method, and we use $\psi_\sigma(\boldsymbol{x})$ and $\psi_\sigma^+(\boldsymbol{x})$ as the Schrödinger picture field operators of the effective quasi-particle which describes relative motion of the proton and electron in the atom,

$$|n,\ell,m_\ell,\sigma;t\rangle = |\Psi_{n,\ell,m_\ell,\sigma}(t)\rangle = \int d^3\boldsymbol{x}\,\Psi_{n,\ell,m_\ell}(\boldsymbol{x},t)\psi_\sigma^+(\boldsymbol{x})|0\rangle.$$

Stated differently, $\psi_\sigma(\boldsymbol{x})$ and $\psi_\sigma^+(\boldsymbol{x})$ are the Schrödinger picture field operators which arise from quantization of the wave function $\langle\boldsymbol{x},\sigma|\Psi(t)\rangle$ which described relative motion in Schrödinger's wave mechanics.
According to our results from Section 18.4, the Hamiltonian (18.39) includes an approximation if we use it for coupling the electromagnetic potential to the hydrogen atom, because we introduced the photon operators through minimal coupling into the effective single particle problem that resulted from separation of the center of mass motion. This is a good approximation if the electromagnetic potentials vary only weakly over the size of the atom, $\boldsymbol{A}(\boldsymbol{x}_p,t) \simeq \boldsymbol{A}(\boldsymbol{x}_e,t)$. Indeed, it is an excellent approximation for the study of transitions between bound hydrogen states, because in these cases $\lambda > hc/13.6\,\mathrm{eV} = 91\,\mathrm{nm}$.
The relevant transition matrix elements for photon emission between t' and t are

$$\begin{aligned}
S_{fi}(t,t') &\equiv S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma}(t,t') \\
&= \langle n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha;t|\exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right)|n,\ell,m_\ell,\sigma;0;t'\rangle \\
&= \langle n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{t'}^{t}d\tau H_D(\tau)\right)|n,\ell,m_\ell,\sigma;0\rangle \\
&\quad\times|n,\ell,m_\ell,\sigma;0\rangle,
\end{aligned}$$

where

$$H_D(\tau) = \exp\left(\frac{\mathrm{i}}{\hbar}H_0\tau\right)(H_I + H_{II})\exp\left(-\frac{\mathrm{i}}{\hbar}H_0\tau\right).$$

The entries $(\boldsymbol{k},\alpha)$ and 0 after the semi-colons in the states refer to a photon of momentum $\hbar\boldsymbol{k}$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ in the final state, and no photon in the initial state.
The scattering matrix element is in leading order

$$\begin{aligned}
S_{fi} &= S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma} = \langle n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|U_D(\infty,-\infty)|n,\ell,m_\ell,\sigma;0\rangle \\
&\simeq \frac{1}{\mathrm{i}\hbar}\int_{-\infty}^{\infty}dt\,\exp\left[\mathrm{i}(\omega_{n',\ell';n,\ell}+ck)t\right]\langle n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha| \\
&\quad\times\int d^3\boldsymbol{x}\sum_\nu\frac{\mathrm{i}q\hbar}{2m}\boldsymbol{A}(\boldsymbol{x})\cdot\left(\psi_\nu^+(\boldsymbol{x})\overset{\leftrightarrow}{\boldsymbol{\nabla}}\psi_\nu(\boldsymbol{x})\right)|n,\ell,m_\ell,\sigma;0\rangle \qquad (18.40)
\end{aligned}$$

with the field operators in the Schrödinger picture. We also took into account that the energy levels are ℓ dependent through fine structure. At this stage we

are still using $\boldsymbol{A}(\boldsymbol{x})$, although our reasoning in Section 18.4 already indicated that any $\boldsymbol{x}$ dependence in $\boldsymbol{A}(\boldsymbol{x})$ must be negligible to justify minimal photon coupling into the effective Hamiltonian for relative motion in the atom. We will return to this point below.

Substitution of the mode expansion (18.20) for the photon operator and evaluation of the second quantized matrix element transforms the transition matrix element for photon emission into a matrix element of first quantized theory,

$$S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma} \simeq 2\pi\delta(\omega_{n',\ell';n,\ell} + ck)\frac{\mathrm{i}q}{m\hbar}\sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\delta_{\sigma\sigma'} \times\langle n',\ell',m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}\exp(-\mathrm{i}\boldsymbol{k}\cdot\mathbf{x})|n,\ell,m_\ell\rangle. \quad (18.41)$$

The operators $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}$ and $\boldsymbol{k}\cdot\mathbf{x}$ commute, whence we don't encounter a normal ordering problem in the first quantized matrix element.

Equation (18.41) can be interpreted as a first quantized matrix element of the perturbation operator

$$V(t) = -\frac{q}{2m}\left(\mathbf{p}\cdot\boldsymbol{A}(\mathbf{x},t) + \boldsymbol{A}(\mathbf{x},t)\cdot\mathbf{p}\right), \quad (18.42)$$

which contains an operator corresponding to a classical transversely polarized plane wave

$$\boldsymbol{A}^{(+)}_\alpha(\boldsymbol{x},t) = \sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - ckt)]. \quad (18.43)$$

This classical plane wave apparently represents a single *emitted* photon of sharp energy $\hbar ck$ and momentum $\hbar\boldsymbol{k}$, and second quantization helped us to determine both the proper amplitude for the single photon wave and the $\boldsymbol{k}$-dependent term in the transition matrix element. The corresponding calculation for *absorption* of a photon yields a first quantized matrix element of the perturbation operator (18.42) with a single photon vector potential

$$\boldsymbol{A}^{(-)}_\alpha(\boldsymbol{x},t) = \sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - ckt)], \quad (18.44)$$

see equation (18.55).

We can understand the amplitudes of the single photon wave functions (18.43) and (18.44) in the following way: The mode expansion (18.20) becomes in finite volume V

$$\boldsymbol{A}(\boldsymbol{x},t) = \sqrt{\frac{\hbar\mu_0 c}{V}}\sum_{\boldsymbol{k}}\sum_{\alpha=1}^{2}\frac{\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})}{\sqrt{2k}}\Big(a_\alpha(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - ckt)] + a^+_\alpha(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - ckt)]\Big), \quad (18.45)$$

and the corresponding energy and momentum operators[2] are

$$H = \sum_{\boldsymbol{k}}\sum_{\alpha}\hbar ck\, a^+_\alpha(\boldsymbol{k})a_\alpha(\boldsymbol{k}), \quad \boldsymbol{P} = \sum_{\boldsymbol{k}}\sum_{\alpha}\hbar\boldsymbol{k}\, a^+_\alpha(\boldsymbol{k})a_\alpha(\boldsymbol{k}).$$

[2] Classically these equations would hold for time averages.

These equations tell us for a classical amplitude $a_\alpha(\boldsymbol{k})$ that this amplitude would (up to an arbitrary phase φ) have to be a Kronecker δ with respect to momentum and polarization to represent a single photon of momentum $\hbar\boldsymbol{k}$, energy $\hbar ck$ and polarization $\boldsymbol{\epsilon}_\alpha$, and therefore the classical vector potential for the single photon in the continuum limit $V \to 8\pi^3$ is

$$\begin{aligned}\boldsymbol{A}_{\gamma,\boldsymbol{k},\alpha}(\boldsymbol{x},t) &= \sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\Big(\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt+\varphi)] \\ &\quad +\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt+\varphi)]\Big) \\ &= 2\sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cos(\boldsymbol{k}\cdot\boldsymbol{x}-ckt+\varphi). \qquad (18.46)\end{aligned}$$

Note however that for emission only the plane wave with $\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-ckt+\varphi)]$ contributes to the transition matrix element, whereas for absorption only the other term contributes.

The vector potential in box normalization (18.45) does have the expected units Vs/m, whereas the continuum limit vector potentials (18.20,18.46) come in units of $\mathrm{m}^{3/2}$Vs/m. This is related to the fact that their transition matrix elements squared yield transition probability densities per volume unit $d^3\boldsymbol{k}$ in the photon state space, see e.g. equation (18.47) below. It is the same effect that we encountered in scattering theory for momentum eigenstates $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})/V^{1/2}$ in box normalization or $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})/(2\pi)^{3/2}$ in the continuum limit.

Evaluation of the transition matrix element in the dipole approximation

We have already emphasized that the coupling of the electromagnetic potentials to the effective single particle model for relative motion in atoms assumes a long wavelength approximation in the sense $\boldsymbol{A}(\boldsymbol{x}_p,t) \simeq \boldsymbol{A}(\boldsymbol{x}_e,t)$, see equations (18.35) and (18.38). Therefore the exponential factor $\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})$ must effectively be constant over the extension of the atomic wave functions and can be replaced by $\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \simeq 1$. For an estimate of the product $|\boldsymbol{k}\cdot\boldsymbol{x}|$, we recall that the energy of the emitted photon from an excited bound state cannot exceed the binding energy of hydrogen,

$$\frac{hc}{\lambda} < -E_1 = \frac{e^2}{8\pi\epsilon_0 a_0} = \frac{hc\alpha}{4\pi a_0},$$

and therefore

$$\lambda > \frac{4\pi}{\alpha}a_0 \simeq 1.72\times 10^3 a_0, \quad ka_0 < \frac{\alpha}{2} \simeq 3.65\times 10^{-3}.$$

This confirms that the exponential factor will be approximately constant over the extension of the wave functions,

$$\langle n',\ell',m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}\exp(-\mathrm{i}\boldsymbol{k}\cdot\mathbf{x})|n,\ell,m_\ell\rangle \approx \langle n',\ell',m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}|n,\ell,m_\ell\rangle.$$

The matrix element of the momentum operator between energy eigenstates is usually converted into matrix elements of the position operator $\mathbf{x}$ using the first quantized Hamiltonian $H_0 = (\mathbf{p}^2/2m) + V(\mathbf{x})$ and the relation

$$[H_0, \mathbf{x}] = \frac{\hbar}{\mathrm{i}m}\mathbf{p}.$$

This implies

$$\begin{aligned}\langle n', \ell', m'_\ell|\mathbf{p}|n, \ell, m_\ell\rangle &= \mathrm{i}\frac{m}{\hbar}\langle n', \ell', m'_\ell|[H_0, \mathbf{x}]|n, \ell, m_\ell\rangle \\ &= \mathrm{i}m\omega_{n',\ell';n,\ell}\langle n', \ell', m'_\ell|\mathbf{x}|n, \ell, m_\ell\rangle,\end{aligned}$$

where $\hbar\omega_{n',\ell';n,\ell} = E_{n',\ell'} - E_{n,\ell}$. In the case of emission we have $\omega_{n',\ell';n,\ell} < 0$. The transition matrix element (18.41) therefore becomes

$$\begin{aligned}S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma} &\simeq -2\pi\delta(\omega_{n',\ell';n,\ell} + ck)q\sqrt{\frac{\mu_0 c}{16\pi^3\hbar k}}\delta_{\sigma\sigma'}\omega_{n',\ell';n,\ell} \\ &\quad\times\langle n', \ell', m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n, \ell, m_\ell\rangle \\ &= \delta(\omega_{n',\ell';n,\ell} + ck)q\sqrt{\frac{\mu_0 c^3 k}{4\pi\hbar}}\delta_{\sigma\sigma'} \\ &\quad\times\langle n', \ell', m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n, \ell, m_\ell\rangle.\end{aligned}$$

The differential emission rate into a momentum volume element $d^3\boldsymbol{k}$ around $\boldsymbol{k}$ of a photon of polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ is then with $q = -e$, $\delta(0) \to T/2\pi$,

$$\begin{aligned}d\Gamma^{(\alpha)}(\boldsymbol{k})_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} &= d^3\boldsymbol{k}\frac{\left|S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma}\right|^2}{T} \\ &\simeq \frac{\mu_0 c^3 e^2}{8\pi^2\hbar}k\delta_{\sigma\sigma'}\left|\langle n', \ell', m'_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n, \ell, m_\ell\rangle\right|^2 \\ &\quad\times\delta(\omega_{n,\ell;n',\ell'} - ck)d^3\boldsymbol{k}, \qquad (18.47)\end{aligned}$$

or after integration over the wavenumber k of the emitted photon,

$$\begin{aligned}\frac{d\Gamma^{(\alpha)}(\hat{\boldsymbol{k}})_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'}}{d\Omega} &= \frac{\mu_0 e^2}{8\pi^2\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'} \\ &\quad\times\left|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n', \ell', m'_\ell|\mathbf{x}|n, \ell, m_\ell\rangle\right|^2.\end{aligned}$$

Note that if we would have tried to calculate this only within a semi-classical first quantized theory for the monochromatic perturbation (18.42,18.43), the δ function in energy and the units of the transition matrix element would have tempted us to introduce a density $\varrho(E_{n'})$ of final hydrogen states per energy and volume, similar to the Golden Rule for transitions into a continuum. This factor would then have appeared instead of the factor $\delta(E_n - E_{n'} - \hbar ck)d^3\boldsymbol{k}$ in (18.47). Indeed, we do have a transition into a continuum of final *photon* states, but the semi-classical approximation would have missed that and naive application of the Golden Rule would have tempted us to include a wrong factor with an unjustified interpretation.

As a consequence of the φ dependence of the spherical harmonics, the vector

$$\begin{aligned}\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle &= \langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x + \langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y\\ &\quad+\langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle\boldsymbol{e}_z\\ &= \langle n',\ell',m'_\ell|r\sin\vartheta\cos\varphi|n,\ell,m_\ell\rangle\boldsymbol{e}_x\\ &\quad+\langle n',\ell',m'_\ell|r\sin\vartheta\sin\varphi|n,\ell,m_\ell\rangle\boldsymbol{e}_y\\ &\quad+\langle n',\ell',m'_\ell|r\cos\vartheta|n,\ell,m_\ell\rangle\boldsymbol{e}_z\end{aligned}$$

has real x and z components and an imaginary y component. We know already from the dipole selection rules from Section 15.1 that the z component $\langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle$ is only different from 0 if $\Delta m_\ell = m'_\ell - m_\ell = 0$, while the x and y components are only different from 0 if $\Delta m_\ell = \pm 1$.
The different conjugation properties and selection rules imply

$$\begin{aligned}&|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle|^2 = \Big(\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\left[\langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x\right.\\ &\left.-\langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y + \langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle\boldsymbol{e}_z\right]\Big)\\ &\times\Big(\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\left[\langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x + \langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y\right.\\ &\left.+\langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle\boldsymbol{e}_z\right]\Big)\\ &= \left[\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x\right]^2 + \left[\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle\boldsymbol{e}_z\right]^2\\ &\quad+\left[\mathrm{i}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y\right]^2.\end{aligned}$$

This cannot be directly associated with an angle between the polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ and one of the real vectors

$$\begin{aligned}\langle n',\ell',m'_\ell|\mathbf{x}_\pm|n,\ell,m_\ell\rangle &= \langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x \pm \mathrm{i}\langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y\\ &\quad+\langle n',\ell',m'_\ell|\mathrm{z}|n,\ell,m_\ell\rangle\boldsymbol{e}_z\end{aligned}$$

because of missing cross terms of the form

$$\pm 2\left[\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{x}|n,\ell,m_\ell\rangle\boldsymbol{e}_x\right]\left[\mathrm{i}\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathrm{y}|n,\ell,m_\ell\rangle\boldsymbol{e}_y\right].$$

However, we can write

$$\begin{aligned}|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle|^2 &= \frac{1}{2}\,|\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle|^2\\ &\quad\times\left(\cos^2\theta_{\alpha,-}+\cos^2\theta_{\alpha,+}\right)\end{aligned}$$

where $\theta_{\alpha,-}$ and $\theta_{\alpha,+}$ are the angles between the polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ and the real vectors $\langle n',\ell',m'_\ell|\mathbf{x}_-|n,\ell,m_\ell\rangle$ and $\langle n',\ell',m'_\ell|\mathbf{x}_+|n,\ell,m_\ell\rangle$, respectively.
This yields a differential emission rate

$$\begin{aligned}d\Gamma^{(\alpha)}(\hat{\boldsymbol{k}})_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} &= \frac{\mu_0 e^2}{8\pi^2\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\,|\langle n',\ell',m'_\ell|\mathbf{x}|n,\ell,m_\ell\rangle|^2\\ &\quad\times\frac{\cos^2\theta_{\alpha,-}+\cos^2\theta_{\alpha,+}}{2}\,d\Omega.\end{aligned}\tag{18.48}$$

The solid angle element $d\Omega = \sin\vartheta\, d\vartheta d\varphi$ measures the direction of the emission vector $\boldsymbol{k}$ and the calculation of the total polarized emission rate $\Gamma^{(\alpha)}_{n,\ell,m_\ell\to n',\ell',m'_\ell}$ requires integration over $d\Omega$. We can do that e.g. by evaluating the angles $\theta_{\alpha,\pm}$ in terms of the angles $\{\vartheta_\alpha, \varphi_\alpha\}$ of the vector $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ and the angles $\{\vartheta_\pm, \varphi_\pm\}$ of the vectors $\langle n', \ell', m'_\ell|\mathbf{x}_\pm|n, \ell, m_\ell\rangle$. However, a faster way is to choose in each of the two terms the respective angle $\theta_{\alpha,\pm}$ and a corresponding azimuthal angle $\phi_{\alpha,\pm}$ as integration variables. This reduces the calculation of the angular integrals to

$$\int_0^{2\pi} d\phi_{\alpha,\pm} \int_0^{\pi} d\theta_{\alpha,\pm}\, \sin\theta_{\alpha,\pm}\, \cos^2\theta_{\alpha,\pm} = \frac{4\pi}{3}.$$

The total emission rate for *polarized* photons is therefore

$$\Gamma^{(\alpha)}_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} = \frac{\mu_0 e^2}{6\pi\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\left|\langle n', \ell', m'_\ell|\mathbf{x}|n, \ell, m_\ell\rangle\right|^2, \tag{18.49}$$

and the total unpolarized emission rate is

$$\Gamma_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} = \frac{\mu_0 e^2}{3\pi\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\left|\langle n', \ell', m'_\ell|\mathbf{x}|n, \ell, m_\ell\rangle\right|^2. \tag{18.50}$$

The relation $\Gamma_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} = 2\Gamma^{(\alpha)}_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'}$ follows at a more formal level from the fact that

$$\sum_{\alpha=1}^{2} \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \otimes \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) = \underline{\mathbf{1}} - \hat{\boldsymbol{k}} \otimes \hat{\boldsymbol{k}}$$

is the projector onto the plane orthogonal to $\boldsymbol{k}$, and therefore

$$\sum_\alpha \left|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \cdot \langle n', \ell', m'_\ell|\mathbf{x}_\pm|n, \ell, m_\ell\rangle\right|^2 = \left|\langle n', \ell', m'_\ell|\mathbf{x}|n, \ell, m_\ell\rangle\right|^2 \sin^2\theta_\pm,$$

where $\theta_\pm$ are the angles between the wave vector $\boldsymbol{k}$ and the two real vectors $\langle n', \ell', m'_\ell|\mathbf{x}_\pm|n, \ell, m_\ell\rangle$. Therefore we find for the unpolarized differential emission rate

$$\begin{aligned} d\Gamma(\hat{\boldsymbol{k}})_{n,\ell,m_\ell,\sigma\to n',\ell',m'_\ell,\sigma'} &= \frac{\mu_0 e^2}{8\pi^2\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\left|\langle n', \ell', m'_\ell|\mathbf{x}|n, \ell, m_\ell\rangle\right|^2 \\ &\quad \times \frac{\sin^2\theta_- + \sin^2\theta_+}{2}\, d\Omega, \end{aligned} \tag{18.51}$$

and this time the angular integrals yield

$$\int_0^{2\pi} d\phi_\pm \int_0^{\pi} d\theta_\pm\, \sin^3\theta_\pm = \frac{8\pi}{3},$$

which implies the total emission rate (18.50).
We had to write the polarized and unpolarized differential emission rates (18.48) and (18.51) as averages over two real dipoles $-e\langle n', \ell', m'_\ell|\mathbf{x}_\pm|n, \ell, m_\ell\rangle$,

where we used the dipole selection rules for hydrogen states. For general atomic or molecular states, all Cartesian components of $\langle f|\mathbf{x}|i\rangle$ may be complex, and we may have a sum of two dipoles of different magnitude,

$$\begin{aligned}|\boldsymbol{\epsilon}_\alpha \cdot \langle f|\mathbf{x}|i\rangle|^2 &= (\boldsymbol{\epsilon}_\alpha \cdot \Re\langle f|\mathbf{x}|i\rangle)^2 + (\boldsymbol{\epsilon}_\alpha \cdot \Im\langle f|\mathbf{x}|i\rangle)^2 \\ &= (\Re\langle f|\mathbf{x}|i\rangle)^2 \cos^2\theta_{\alpha,1} + (\Im\langle f|\mathbf{x}|i\rangle)^2 \cos^2\theta_{\alpha,2}, \qquad (18.52)\end{aligned}$$

$$\sum_\alpha |\boldsymbol{\epsilon}_\alpha \cdot \langle f|\mathbf{x}|i\rangle|^2 = (\Re\langle f|\mathbf{x}|i\rangle)^2 \sin^2\theta_1 + (\Im\langle f|\mathbf{x}|i\rangle)^2 \sin^2\theta_2.$$

This yields the same results as (18.48) in a different parametrization. The difference between the construction in (18.48) and (18.52) is that we could construct two dipoles of the same magnitude $-e\,|\langle n', \ell', m'_\ell|\mathbf{x}|n, \ell, m_\ell\rangle|$ in (18.48) and express the result as an average, whereas the generic construction (18.52) yields a sum of two dipoles of different magnitude.

Since we are observing photons of certain frequency with no regard to the particular transition which generated those photons, it is customary to sum the emission rate over degenerate final states and average over degenerate initial states. The emission rate per excited atom for photons with angular frequency $\omega_{n,\ell;n',\ell'}$ follows from (18.50) as

$$\begin{aligned}\Gamma_{n,\ell\to n',\ell'} &= \frac{1}{2\ell+1} \sum_{m_\ell=-\ell}^{\ell} \sum_{m'_\ell=-\ell'}^{\ell'} \Gamma_{n,\ell,m_\ell\to n',\ell',m'_\ell} \\ &= \frac{\mu_0 e^2}{2\pi m c} \omega^2_{n,\ell;n',\ell'} \left|f_{n',\ell'|n,\ell}\right|. \qquad (18.53)\end{aligned}$$

Here we have set $\sigma = \sigma'$ and omitted the spin indices, and we used the definition (15.25) of the averaged oscillator strength.

The quantity $\Gamma_{n,\ell\to n',\ell'} \equiv A_{n,\ell\to n',\ell'}$ provides a quantum mechanical expression for the Einstein A coefficient for spontaneous emission of photons. Einstein had introduced this coefficient in 1916 in his balance equations for the origin of the Planck spectrum.

We have seen that in leading order the relevant interaction Hamiltonian for photon emission or absorption is

$$H_I = \int d^3\boldsymbol{x} \sum_\sigma \mathrm{i}\frac{q\hbar}{2m} \boldsymbol{A} \cdot \left(\psi^+_\sigma \overleftrightarrow{\boldsymbol{\nabla}} \psi_\sigma\right),$$

and in the Schrödinger picture this operator contains only time-independent field operators $\boldsymbol{A}(\boldsymbol{x})$, $\psi_\sigma(\boldsymbol{x})$.

Substitution of the mode expansions in terms of the momentum space operators yields (note $q \neq |\boldsymbol{q}|$ in the following equation):

$$\begin{aligned}H_I = &-\frac{q\hbar}{m}\sqrt{\frac{\hbar\mu_0 c}{(2\pi)^3}} \int \frac{d^3\boldsymbol{q}}{\sqrt{2|\boldsymbol{q}|}} \int d^3\boldsymbol{k} \sum_\sigma \sum_\alpha \boldsymbol{k} \cdot \epsilon_\alpha(\boldsymbol{q}) \\ &\times \left(c^+_\sigma(\boldsymbol{k}+\boldsymbol{q}) a_\alpha(\boldsymbol{q}) c_\sigma(\boldsymbol{k}) + c^+_\sigma(\boldsymbol{k}-\boldsymbol{q}) a^+_\alpha(\boldsymbol{q}) c_\sigma(\boldsymbol{k})\right). \qquad (18.54)\end{aligned}$$

The representation of interaction Hamiltonians in terms of $c_\sigma(\boldsymbol{k})$, $c_\sigma^+(\boldsymbol{k})$ is useful for processes involving (quasi-)free electrons, e.g. for the Compton effect ("free-free scattering") or for the discussion of electron-photon interactions in metals (assuming e.g. a jellium model for the electrons). However, for the discussion of emission or absorption from atomic or molecular bound states the $\boldsymbol{x}$-representation is more convenient.

18.6 Photon absorption

We will continue to use energy labels n and n' such that $E_n > E_{n'}$. Therefore the previously discussed transition $n \to n'$ involved photon emission, while the process $n' \to n$ involves photon absorption. Later on we will also compare emission and absorption rates, and it is desirable to make the distinction between emission and absorption rates more visible in the notation. Therefore we will denote absorption rates with the symbol $\tilde{\Gamma}$.
The leading order scattering matrix element for photon absorption due to a transition from a state $|n', \ell', m'_\ell, \sigma'; \boldsymbol{k}, \alpha\rangle$ to a state $|n, \ell, m_\ell, \sigma; 0\rangle$,

$$S_{n,\ell,m_\ell,\sigma|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha} \simeq \frac{1}{\mathrm{i}\hbar}\int_{-\infty}^{\infty} dt\, \exp\left[\mathrm{i}(\omega_{n,\ell;n',\ell'} - ck)t\right]$$
$$\times\langle n, \ell, m_\ell, \sigma; 0|\int d^3\boldsymbol{x} \sum_\nu \mathrm{i}\frac{q\hbar}{2m}\boldsymbol{A}(\boldsymbol{x})\cdot\left(\psi_\nu^+(\boldsymbol{x})\overset{\leftrightarrow}{\boldsymbol{\nabla}}\psi_\nu(\boldsymbol{x})\right)|n', \ell', m'_\ell, \sigma'; \boldsymbol{k}, \alpha\rangle$$

is just the negative complex conjugate of the emission matrix element (18.40). The resulting scattering matrix element after evaluation of the field operators,

$$S_{n,\ell,m_\ell,\sigma|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha} \simeq 2\pi\delta(\omega_{n,\ell;n',\ell'} - ck)\frac{\mathrm{i}q}{m\hbar}\sqrt{\frac{\hbar\mu_0 c}{16\pi^3 k}}\delta_{\sigma\sigma'}$$
$$\times\langle n, \ell, m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{p}\exp(\mathrm{i}\boldsymbol{k}\cdot\mathbf{x})|n', \ell', m'_\ell\rangle, \qquad (18.55)$$

therefore has the form of a first quantized scattering matrix element with perturbation (18.42) and vector potential (18.44).
The equality of the scattering matrix elements up to a phase factor also implies that the absorption rate per $\boldsymbol{k}$ space volume of the incoming photons has the same value as the corresponding emission rate (18.47) per $\boldsymbol{k}$ space volume of emitted photons,

$$\frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell,\sigma'\to n,\ell,m_\ell,\sigma}}{d^3\boldsymbol{k}} = \frac{\left|S_{n,\ell,m_\ell,\sigma|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha}\right|^2}{T}$$
$$\simeq \frac{\mu_0 c^3 e^2}{8\pi^2\hbar}k\delta_{\sigma\sigma'}\left|\langle n, \ell, m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n', \ell', m'_\ell\rangle\right|^2$$
$$\times\delta(\omega_{n,\ell;n',\ell'} - ck), \qquad (18.56)$$

where $q = -e$ was substituted.

This yields the differential absorption rate for polarized photons in terms of the angles $\theta_{\alpha,\pm}$ between the vectors $\langle n,\ell,m_\ell|\mathbf{x}_\pm|n',\ell',m'_\ell\rangle$ and the polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$,

$$\frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell,\sigma'\to n,\ell,m_\ell,\sigma}}{d^3\boldsymbol{k}} \simeq \frac{\mu_0 c^3 e^2}{8\pi^2\hbar} k\delta_{\sigma\sigma'} \left|\langle n,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2 \times\frac{\cos^2\theta_{\alpha,-}+\cos^2\theta_{\alpha,+}}{2}\delta(\omega_{n,\ell;n',\ell'}-ck).$$

The differential absorption rate for unpolarized photons depends on the angles $\theta_\pm$ between the vectors $\langle n,\ell,m_\ell|\mathbf{x}_\pm|n',\ell',m'_\ell\rangle$ and the incident vector $\boldsymbol{k}$,

$$\begin{aligned}\frac{d\tilde{\Gamma}(\boldsymbol{k})_{n',\ell',m'_\ell,\sigma'\to n,\ell,m_\ell,\sigma}}{d^3\boldsymbol{k}} &= \sum_\alpha \frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell,\sigma'\to n,\ell,m_\ell,\sigma}}{d^3\boldsymbol{k}} \\ &\simeq \frac{\mu_0 c^3 e^2}{8\pi^2\hbar} k\delta_{\sigma\sigma'} \left|\langle n,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2 \\ &\quad\times\frac{\sin^2\theta_-+\sin^2\theta_+}{2}\delta(\omega_{n,\ell;n',\ell'}-ck). \end{aligned} \tag{18.57}$$

The total absorption rate between the specified states follows as

$$\tilde{\Gamma}_{n',\ell',m'_\ell,\sigma'\to n,\ell,m_\ell,\sigma} = \frac{\mu_0 e^2}{3\pi\hbar c}\omega^3_{n,\ell;n',\ell'}\delta_{\sigma\sigma'}\left|\langle n,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle\right|^2, \tag{18.58}$$

and the total absorption rate per atom for photons of angular frequency $\omega_{n,\ell;n',\ell'}$ is

$$\begin{aligned}\tilde{\Gamma}_{n',\ell'\to n,\ell} &= \frac{1}{2\ell'+1}\sum_{m'_\ell=-\ell'}^{\ell'}\sum_{m_\ell=-\ell}^{\ell}\tilde{\Gamma}_{n',\ell',m'_\ell\to n,\ell,m_\ell} \\ &= \frac{\mu_0 e^2}{2\pi mc}\omega^2_{n,\ell;n',\ell'} f_{n,\ell|n',\ell'}. \end{aligned} \tag{18.59}$$

This differs from the corresponding spontaneous emission rate (18.53) for photons of angular frequency $\omega_{n,\ell;n',\ell'}$ only through the different averaging factors for the respective initial states,

$$\tilde{\Gamma}_{n',\ell'\to n,\ell} = \frac{2\ell+1}{2\ell'+1}\Gamma_{n,\ell\to n',\ell'}. \tag{18.60}$$

The number of absorption events will be proportional to the flux of incoming photons, and therefore another observable of interest is the absorption rate per flux of incoming photons, i.e. the absorption cross section.

The *photon flux* or current density of monochromatic photons of momentum $\hbar\boldsymbol{k}$ can be calculated by dividing their energy current density $\boldsymbol{\mathcal{S}}(\boldsymbol{k})$ by their energy $\hbar ck$. Equations (18.21,18.22,18.29) and (18.46) yield

$$\frac{\boldsymbol{\mathcal{S}}(\boldsymbol{k})}{\hbar ck} = \frac{\boldsymbol{E}\times\boldsymbol{B}}{\mu_0\hbar ck} = \frac{c}{(2\pi)^3}\hat{\boldsymbol{k}}. \tag{18.61}$$

This is actually a photon flux $d\boldsymbol{j}(\boldsymbol{k})/d^3\boldsymbol{k}$ per $\boldsymbol{k}$ space volume due to the use of the photon wave functions in the continuum limit[3].
Equations (18.56) and (18.61) yield the polarized photon absorption cross section

$$\begin{aligned}\sigma^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to n,\ell,m_\ell} &= \frac{d\tilde{\Gamma}^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to n,\ell,m_\ell}}{dj(\boldsymbol{k})} \\ &\simeq \frac{\pi\mu_0 ce^2}{\hbar}\omega_{n,\ell;n',\ell'}\,|\langle n,\ell,m_\ell|\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})\cdot\mathbf{x}|n',\ell',m'_\ell\rangle|^2 \\ &\quad\times\delta(\omega_{n,\ell;n',\ell'}-ck). \end{aligned} \tag{18.62}$$

To average this over the angles of the incident photons, we can use the same methods that we applied for the calculation of the total polarized emission rate (18.49), except for an extra factor of $(4\pi)^{-1}$ from the averaging over directions. This yields an isotropic cross section for polarized photons

$$\sigma^{(\alpha)}(k)_{n',\ell',m'_\ell\to n,\ell,m_\ell} = \frac{1}{2}\sigma(k)_{n',\ell',m'_\ell\to n,\ell,m_\ell}$$

and a total isotropic cross section

$$\sigma(k)_{n',\ell',m'_\ell\to n,\ell,m_\ell} \simeq \frac{2\pi\mu_0 ce^2}{3\hbar}\omega_{n,\ell;n',\ell'}\,|\langle n,\ell,m_\ell|\mathbf{x}|n',\ell',m'_\ell\rangle|^2\,\delta(\omega_{n,\ell;n',\ell'}-ck).$$

The average absorption cross section per atom for photons of angular frequency $\omega_{n,\ell;n',\ell'}$ follows then again through averaging over initial states and summation over final states,

$$\begin{aligned}\sigma(k)_{n',\ell'\to n,\ell} &= \frac{1}{2\ell'+1}\sum_{m'_\ell=-\ell'}^{\ell'}\sum_{m_\ell=-\ell}^{\ell}\sigma(k)_{n',\ell',m'_\ell\to n,\ell,m_\ell} \\ &= \frac{\pi\mu_0 ce^2}{m}f_{n,\ell|n',\ell'}\delta(\omega_{n,\ell;n',\ell'}-ck). \end{aligned} \tag{18.63}$$

We get a more realistic representation for absorption cross secctions if we take into account the representation (2.10) of the δ function,

$$\begin{aligned}\delta(\omega_{n,\ell;n',\ell'}-ck) &= \lim_{\gamma\to 0}\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,\exp[\mathrm{i}(\omega_{n,\ell;n',\ell'}-ck)t-\gamma|t|] \\ &= \lim_{\gamma\to 0}\frac{1}{\pi}\frac{\gamma}{(\omega_{n,\ell;n',\ell'}-ck)^2+\gamma^2}. \end{aligned} \tag{18.64}$$

Keeping a finite value of γ yields a Lorentzian absorption line shape of half width 2γ,

$$\sigma(k)_{n',\ell'\to n,\ell} = \frac{\mu_0 ce^2}{m}f_{n,\ell|n',\ell'}\frac{\gamma}{(\omega_{n,\ell;n',\ell'}-ck)^2+\gamma^2}. \tag{18.65}$$

[3]The result in box normalization is $\boldsymbol{j}(\boldsymbol{k}) = (c/V)\hat{\boldsymbol{k}}$.

A finite width of line shapes arises from many sources. A certainly not exhaustive list of mechanisms includes adiabatic switching of perturbations, lifetime broadening, pressure broadening, Doppler broadening, and broadening through chemical shifts.
We have found $\Gamma \propto \delta_{\sigma\sigma'}$ both for photon emission and absorption, i.e. no spin-flips in either process. The same holds in arbitrary order with the Hamiltonian (18.39), since there are no spin flipping terms there. How then can a magnetic field flip spins even for non-relativistic electrons? There is actually a term missing in the Hamiltonian (18.39), the Pauli term:

$$H_B = -\frac{q}{m}\int d^3\boldsymbol{x} \sum_{\sigma,\sigma'} \psi^+_\sigma(\boldsymbol{x}) \boldsymbol{S}_{\sigma,\sigma'} \cdot (\boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{x}))\psi_{\sigma'}(\boldsymbol{x}). \tag{18.66}$$

This term induces spin flips through two of the three components of the vector of Pauli matrices $\underline{\boldsymbol{S}} = \hbar\underline{\boldsymbol{\sigma}}/2$, and it follows from a systematic non-relativistic expansion of the relativistic wave equation for electrons, see Chapter 21. We could neglect the Pauli term in the present calculation, because a derivative on the vector potential yields a factor k, whereas a derivative on the wave functions amounts approximately to a factor of order $1/a_0$. The Pauli term is therefore suppressed relative to H_I by approximately $ka_0 < \alpha/2$.

18.7 Stimulated emission of photons

Here we use box normalization in a volume $V = L^3$, i.e. $\boldsymbol{k} = 2\pi\boldsymbol{n}/L$.
If we have already $n_{\boldsymbol{k},\alpha}$ photons of momentum $\hbar\boldsymbol{k}$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ in the initial state,

$$|n,\ell,m_\ell,\sigma;n_{\boldsymbol{k},\alpha}\rangle = \int d^3\boldsymbol{x}\, \psi^+_\sigma(\boldsymbol{x}) \frac{(a^+_\alpha(\boldsymbol{k}))^{n_{\boldsymbol{k},\alpha}}}{\sqrt{n_{\boldsymbol{k},\alpha}!}} |0\rangle \langle \boldsymbol{x}|n,\ell,m_\ell\rangle,$$

the basic oscillator relation $\langle n+1|a^+|n\rangle = \sqrt{n+1}$ yields for the leading order scattering matrix elements the relation

$$S_{n',\ell',m'_\ell,\sigma';n_{\boldsymbol{k},\alpha}+1|n,\ell,m_\ell,\sigma;n_{\boldsymbol{k},\alpha}} = \sqrt{n_{\boldsymbol{k},\alpha}+1} S_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma},$$

i.e. the emission rate scales with the number of photons of momentum $\hbar\boldsymbol{k}$, energy $\hbar ck = \hbar\omega_{n,\ell;n',\ell'}$ and fixed polarization like

$$\begin{aligned}
\Gamma^{(\alpha)}_{n,\ell;n_{\boldsymbol{k},\alpha}\to n',\ell';n_{\boldsymbol{k},\alpha}+1} &= (n_{\boldsymbol{k},\alpha}+1)\Gamma^{(\alpha)}_{n,\ell;0\to n',\ell';1} \\
&= \frac{n_{\boldsymbol{k},\alpha}+1}{2\ell+1} \sum_{m_\ell=-\ell}^{\ell} \sum_{m'_\ell=-\ell'}^{\ell'} \Gamma^{(\alpha)}_{n,\ell,m_\ell\to n',\ell',m'_\ell} \\
&= (n_{\boldsymbol{k},\alpha}+1)\frac{\mu_0 e^2}{4\pi mc}\omega^2_{n,\ell;n',\ell'} \left|f_{n',\ell'|n,\ell}\right|.
\end{aligned}$$

The total polarized emission rate in the presence of the $n_{\boldsymbol{k},\alpha}$ photons therefore differs from the "spontaneous" emission rate $\Gamma^{(\alpha)}_{n,\ell;0\to n',\ell';1} \equiv \Gamma^{(\alpha)}_{n,\ell\to n',\ell'} = \Gamma_{n,\ell\to n',\ell'}/2$ (cf. equation (18.53)) by an additional "stimulated" emission rate

$$\Gamma^{(s,\alpha)}_{n,\ell;n_{\boldsymbol{k},\alpha}\to n',\ell';n_{\boldsymbol{k},\alpha}+1} = n_{\boldsymbol{k},\alpha}\Gamma^{(\alpha)}_{n,\ell;0\to n',\ell';1} = n_{\boldsymbol{k},\alpha}\frac{\mu_0 e^2}{4\pi mc}\omega^2_{n,\ell;n',\ell'}\left|f_{n',\ell'|n,\ell}\right|$$

which is proportional to the number of photons which are already present in the system. This is sometimes metaphorically explained as a consequence of one of the original photons stimulating the emission by shaking the excited state. However, in the end it is nothing but a combinatorial quantum effect of indistinguishable photon operators.
On the other hand, we find for the absorption of a photon in the initial state

$$|n',\ell',m'_\ell,\sigma';n_{\boldsymbol{k},\alpha}\rangle = \int d^3\boldsymbol{x}\,\psi^+_{\sigma'}(\boldsymbol{x})\frac{(a^+_\alpha(\boldsymbol{k}))^{n_{\boldsymbol{k},\alpha}}}{\sqrt{n_{\boldsymbol{k},\alpha}!}}|0\rangle\langle\boldsymbol{x}|n',\ell',m'_\ell\rangle,$$

from $\langle n-1|a|n\rangle = \sqrt{n}$ the relation

$$\begin{aligned} S_{n,\ell,m_\ell,\sigma;n_{\boldsymbol{k},\alpha}-1|n',\ell',m'_\ell,\sigma';n_{\boldsymbol{k},\alpha}} &= \sqrt{n_{\boldsymbol{k},\alpha}}S_{n,\ell,m_\ell,\sigma|n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha} \\ &= -\sqrt{n_{\boldsymbol{k},\alpha}}S^*_{n',\ell',m'_\ell,\sigma';\boldsymbol{k},\alpha|n,\ell,m_\ell,\sigma}. \end{aligned}$$

Therefore the polarized absorption rate in the presence of $n_{\boldsymbol{k},\alpha}$ photons of momentum $\hbar\boldsymbol{k}$ and polarization $\boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$ is

$$\begin{aligned} &\tilde\Gamma^{(\alpha)}_{n',\ell';n_{\boldsymbol{k},\alpha}\to n,\ell;n_{\boldsymbol{k},\alpha}-1} = n_{\boldsymbol{k},\alpha}\tilde\Gamma^{(\alpha)}_{n',\ell';1\to n,\ell;0} \\ &= \frac{n_{\boldsymbol{k},\alpha}}{2\ell'+1}\sum_{m'_\ell=-\ell'}^{\ell'}\sum_{m_\ell=-\ell}^{\ell}\tilde\Gamma^{(\alpha)}_{n',\ell',m'_\ell\to n,\ell,m_\ell} = n_{\boldsymbol{k},\alpha}\frac{\mu_0 e^2}{4\pi mc}\omega^2_{n,\ell;n',\ell'}f_{n,\ell|n',\ell'} \end{aligned}$$

This equals corresponding stimulated and total emission rates up to the different averaging factors for the different initial states which enter into the averaged and summed transition matrix elements,

$$\begin{aligned} \tilde\Gamma^{(\alpha)}_{n',\ell';n_{\boldsymbol{k},\alpha}\to n,\ell;n_{\boldsymbol{k},\alpha}-1} &= \frac{2\ell+1}{2\ell'+1}\Gamma^{(\alpha)}_{n,\ell;n_{\boldsymbol{k},\alpha}-1\to n',\ell';n_{\boldsymbol{k},\alpha}} \\ &= \frac{2\ell+1}{2\ell'+1}\Gamma^{(s,\alpha)}_{n,\ell;n_{\boldsymbol{k},\alpha}\to n',\ell';n_{\boldsymbol{k},\alpha}+1}. \end{aligned}$$

Note that it does not matter that we used the single photon absorption rate and current density in the calculation (18.62) of the polarized photon absorption cross section without explicitly taking into account the number $n_{\boldsymbol{k},\alpha}$ of available photons. The common factor $n_{\boldsymbol{k},\alpha}$ cancels in the ratio

$$\begin{aligned} \sigma^{(\alpha)}(\boldsymbol{k})_{n',\ell',m'_\ell\to n,\ell,m_\ell} &= \frac{d\tilde\Gamma^{(\alpha)}_{n',\ell',m'_\ell;n_{\boldsymbol{k},\alpha}\to n,\ell,m_\ell;n_{\boldsymbol{k},\alpha}-1}}{dJ^{(\alpha)}(\boldsymbol{k})} \\ &= \frac{8\pi^3}{n_{\boldsymbol{k},\alpha}c}\frac{d\tilde\Gamma^{(\alpha)}_{n',\ell',m'_\ell;n_{\boldsymbol{k},\alpha}\to n,\ell,m_\ell;n_{\boldsymbol{k},\alpha}-1}}{d^3\boldsymbol{k}}. \end{aligned}$$

18.8 Photon scattering

For the following calculations we switch back to a generic notation $|n,\zeta\rangle$ for atomic or molecular states, where the energy levels E_n depend on the index set n, and the index set ζ enumerates the degenerate states.
Scattering concerns transitions which involve a photon both in the initial and in the final state: $|n,\zeta;\boldsymbol{k},\alpha\rangle \to |n',\zeta';\boldsymbol{k}',\alpha'\rangle$. Here we consider scattering of photons by bound non-relativistic systems, i.e. the initial state $|n,\zeta\rangle$ and the final state $|n',\zeta'\rangle$ of the scattering system are discrete, and we use minimal coupling of the photon to effective single particle models for relative motion in the bound system. We have seen in Section 18.4 that photon coupling to the relative motion in materials effectively amounts to photon-electron coupling, and therefore we use photon scattering off bound electrons as the relevant paradigm for the following discussion.
To have a non-vanishing matrix element between different 1-photon states in lowest order requires two copies of the photon operator $\boldsymbol{A}$ – one to annihilate the initial photon and one to create the final photon. The relevant interaction Hamiltonian for photon interactions with non-relativistic electrons is

$$\begin{aligned} H_{int} &= \int d^3\boldsymbol{x} \left(-\mathrm{i}\frac{e\hbar}{2m}\boldsymbol{A}\cdot \left(\psi^+ \overset{\leftrightarrow}{\boldsymbol{\nabla}} \psi\right) + \frac{e^2}{2m}\psi^+\boldsymbol{A}^2\psi + \frac{e\hbar}{2m}\psi^+\boldsymbol{\sigma}\cdot\boldsymbol{B}\psi \right) \\ &= H_I + H_{II} + H_B. \end{aligned} \tag{18.67}$$

Summations over spinor indices are tacitly understood. We have already substituted $q = -e$, because we have seen in Section 18.4 that the coupling of long wavelength photons to bound systems involving electrons can effectively be considered as coupling of the photons to a charge $-e$ if the charge binding the electron is $q_2 = e$ or if the mass m_2 of the binding charge is much larger than the electron mass, $m_2 \gg m_e$. The reduced mass m in the Hamiltonian (18.67) is usually also $m \simeq m_e$ in excellent approximation[4].
We can get two copies of $\boldsymbol{A}$ from H_I^2, H_IH_B, H_BH_I and H_B^2 in second order perturbation theory, and from H_{II} in first order perturbation theory. Among these terms, only those involving the Pauli term can induce spin flips. However, we will focus on photon energies in the soft X-ray regime, $E_\gamma \lesssim 1\,\mathrm{keV}$. The allowed transition matrix elements of H_I in the soft X-ray regime are often almost an order of magnitude larger than the allowed matrix elements of H_B, and therefore spin preserving scattering probabilities $|S_{fi}|^2$ of order H_I^4 will be larger by about two orders of magnitude than spin preserving scattering of order $H_I^2H_B^2$ or spin reversing scattering of order $(H_IH_B)^2$.
Therefore we neglect H_B in the following calculations. The relevant scattering

[4] An exception is positronium with $m = m_e/2$.

matrix elements in order $\mathcal{O}(e^2)$ are then

$$\begin{aligned} S_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} &= \langle n',\zeta';\boldsymbol{k}',\alpha'|U_D(\infty,-\infty)|n,\zeta;\boldsymbol{k},\alpha\rangle|_{e^2} \\ &= \langle n',\zeta';\boldsymbol{k}',\alpha'|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty}dt\,H_D(t)\right)|n,\zeta;\boldsymbol{k},\alpha\rangle|_{e^2} \\ &= S^{(I)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} + S^{(II)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}, \end{aligned}$$

with contributions from H_I^2,

$$\begin{aligned} S^{(I)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} = -\frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt'\,\exp[\mathrm{i}(\omega_{n'}+ck')t]\exp[-\mathrm{i}(\omega_n+ck)t'] \\ \times\langle n',\zeta';\boldsymbol{k}',\alpha'|H_I\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(t-t')\right)H_I|n,\zeta;\boldsymbol{k},\alpha\rangle, \end{aligned}$$

and from H_{II},

$$S^{(II)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} = \int_{-\infty}^{\infty}\frac{dt}{\mathrm{i}\hbar}\,\exp[\mathrm{i}(\omega_{n',n}+\omega_{k',k})t]\,\langle n',\zeta';\boldsymbol{k}',\alpha'|H_{II}|n,\zeta;\boldsymbol{k},\alpha\rangle.$$

The first order term $S^{(II)}$ is the easier one to evaluate. Insertion of the mode expansion (18.20) for the photon field yields

$$\begin{aligned} S^{(II)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} &= \frac{\mu_0 ce^2}{8\pi^2\mathrm{i}m\sqrt{kk'}}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\delta(\omega_{n',n}+\omega_{k',k}) \\ &\quad\times\int d^3\boldsymbol{x}\,\exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}]\,\Psi^{+}_{n',\zeta'}(\boldsymbol{x})\Psi_{n,\zeta}(\boldsymbol{x}) \\ &= \frac{\mu_0 ce^2}{8\pi^2\mathrm{i}m\sqrt{kk'}}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\delta(\omega_{n',n}+\omega_{k',k}) \\ &\quad\times\int d^3\boldsymbol{q}\,\Psi^{+}_{n',\zeta'}(\boldsymbol{q}+\boldsymbol{k}-\boldsymbol{k}')\Psi_{n,\zeta}(\boldsymbol{q}). \end{aligned}$$

This leaves in dipole approximation $\exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}]\simeq 1$ the amplitude

$$S^{(II)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} = \frac{\mu_0 e^2}{8\pi^2\mathrm{i}mk}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\delta(k'-k)\delta_{n'n}\delta_{\zeta'\zeta}, \tag{18.68}$$

i.e. only elastic photon scattering, but no Raman scattering from H_{II}.
The term $S^{(I)}$ splits into amplitudes with zero or two photons in virtual intermediate states,

$$S^{(I)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} = S^{(I),0}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} + S^{(I),2}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}.$$

We omit the indices in the amplitudes $S^{(I),0}$ and $S^{(I),2}$ in the following calculations. The amplitude with no photons in the virtual intermediate state is

$$\begin{aligned} S^{(I),0} = \frac{e^2}{4m^2}\sum\!\!\!\!\!\!\int_{n'',\zeta''}\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt'\,\exp[\mathrm{i}(\omega_{n',n''}+ck')t]\exp[\mathrm{i}(\omega_{n'',n}-ck)t'] \\ \times\int d^3\boldsymbol{x}'\,\langle n',\zeta';\boldsymbol{k}',\alpha'|\boldsymbol{A}(\boldsymbol{x}')\cdot\left(\psi^{+}(\boldsymbol{x}')\overset{\leftrightarrow}{\boldsymbol{\nabla}}\psi(\boldsymbol{x}')\right)|n'',\zeta'';0\rangle \\ \times\int d^3\boldsymbol{x}\,\langle n'',\zeta'';0|\boldsymbol{A}(\boldsymbol{x})\cdot\left(\psi^{+}(\boldsymbol{x})\overset{\leftrightarrow}{\boldsymbol{\nabla}}\psi(\boldsymbol{x})\right)|n,\zeta;\boldsymbol{k},\alpha\rangle. \end{aligned}$$

The notation $\sum\!\!\!\!\!\!\int_{n'',\zeta''}$ takes into account that the intermediate states can also be part of the energy continuum of the scattering system.
We have already evaluated the time integrals in second order perturbation terms in (13.31),

$$\int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \, \exp[\mathrm{i}(\omega_{n',n''} + ck')t] \exp[\mathrm{i}(\omega_{n'',n} - ck)t' + \epsilon t'] \\ = -2\pi\mathrm{i}\frac{\delta(\omega_{n',n} + \omega_{k',k})}{\omega_{n'',n} - ck - \mathrm{i}\epsilon}.$$

Evaluation of the matrix elements of the field operators then yields again in dipole approximation $\exp(-\mathrm{i}\boldsymbol{k}' \cdot \boldsymbol{x}') \simeq 1$, $\exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{x}) \simeq 1$ the result

$$S^{(I),0} = \frac{\hbar\mu_0 ce^2}{32\pi^2\mathrm{i}m^2\sqrt{kk'}}\delta(\omega_{n',n} + \omega_{k',k}) \sum\!\!\!\!\!\!\int_{n'',\zeta''} \frac{1}{\omega_{n'',n} - ck - \mathrm{i}\epsilon} \\ \times \int d^3\boldsymbol{x}' \, \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \left(\Psi^+_{n',\zeta'}(\boldsymbol{x}') \overset{\leftrightarrow}{\boldsymbol{\nabla}} \Psi_{n'',\zeta''}(\boldsymbol{x}')\right) \\ \times \int d^3\boldsymbol{x} \, \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) \cdot \left(\Psi^+_{n'',\zeta''}(\boldsymbol{x}) \overset{\leftrightarrow}{\boldsymbol{\nabla}} \Psi_{n,\zeta}(\boldsymbol{x})\right). \tag{18.69}$$

We can transform this from velocity into length form using the by now standard trick $\hbar\mathbf{p} = \mathrm{i}m[H_0, \mathbf{x}]$ to find

$$S^{(I),0} = \frac{\mu_0 ce^2}{8\pi^2\mathrm{i}\hbar\sqrt{kk'}}\delta(\omega_{n',n} + \omega_{k',k}) \sum\!\!\!\!\!\!\int_{n'',\zeta''} \frac{\omega_{n',n''}\omega_{n'',n}}{\omega_{n'',n} - ck - \mathrm{i}\epsilon} \\ \times \langle n', \zeta' | \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \mathbf{x} | n'', \zeta'' \rangle \langle n'', \zeta'' | \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) \cdot \mathbf{x} | n, \zeta \rangle. \tag{18.70}$$

For the amplitude with two photons in the intermediate state we have to take into account that for two-photon states

$$\frac{1}{2}\int d^3\boldsymbol{\kappa}' \int d^3\boldsymbol{\kappa} \sum_{\beta',\beta} |\boldsymbol{\kappa}', \beta'; \boldsymbol{\kappa}, \beta\rangle \langle \boldsymbol{\kappa}', \beta'; \boldsymbol{\kappa}, \beta| = 1.$$

This yields

$$S^{(I),2} = \frac{e^2}{8m^2} \int d^3\boldsymbol{\kappa}' \int d^3\boldsymbol{\kappa} \sum\!\!\!\!\!\!\int_{n'',\zeta''} \sum_{\beta',\beta} \int_{-\infty}^{\infty} dt \int_{-\infty}^{t} dt' \\ \times \exp[\mathrm{i}(\omega_{n',n''} + ck' - c\kappa - c\kappa')t] \exp[\mathrm{i}(\omega_{n'',n} + c\kappa + c\kappa' - ck)t'] \\ \times \int d^3\boldsymbol{x}' \, \langle n', \zeta'; \boldsymbol{k}', \alpha' | \boldsymbol{A}(\boldsymbol{x}') \cdot \left(\psi^+(\boldsymbol{x}') \overset{\leftrightarrow}{\boldsymbol{\nabla}} \psi(\boldsymbol{x}')\right) \\ \times |n'', \zeta''; \boldsymbol{\kappa}', \beta'; \boldsymbol{\kappa}, \beta\rangle \\ \times \int d^3\boldsymbol{x} \, \langle n'', \zeta''; \boldsymbol{\kappa}', \beta'; \boldsymbol{\kappa}, \beta | \boldsymbol{A}(\boldsymbol{x}) \cdot \left(\psi^+(\boldsymbol{x}) \overset{\leftrightarrow}{\boldsymbol{\nabla}} \psi(\boldsymbol{x})\right) | n, \zeta; \boldsymbol{k}, \alpha \rangle.$$

The matrix elements of the photon operators are given by

$$\langle \boldsymbol{\kappa}', \beta'; \boldsymbol{\kappa}, \beta | \boldsymbol{A}(\boldsymbol{x}) | \boldsymbol{k}, \alpha \rangle = \sqrt{\frac{\hbar\mu_0 c}{16\pi^3\kappa}} \boldsymbol{\epsilon}_\beta(\boldsymbol{\kappa}) \exp(-\mathrm{i}\boldsymbol{\kappa} \cdot \boldsymbol{x}) \delta(\boldsymbol{\kappa}' - \boldsymbol{k}) \delta_{\beta'\alpha} \\ + \sqrt{\frac{\hbar\mu_0 c}{16\pi^3\kappa'}} \boldsymbol{\epsilon}_{\beta'}(\boldsymbol{\kappa}') \exp(-\mathrm{i}\boldsymbol{\kappa}' \cdot \boldsymbol{x}) \delta(\boldsymbol{\kappa} - \boldsymbol{k}) \delta_{\beta\alpha}$$

and a corresponding conjugate expression. This yields in dipole approximation

$$\begin{aligned}
&\int d^3\boldsymbol{\kappa}' \int d^3\boldsymbol{\kappa} \sum_{\beta',\beta} \exp[\mathrm{i}c(\kappa+\kappa')(t'-t)] \\
&\times \langle \boldsymbol{k}', \alpha' | \boldsymbol{A}(\boldsymbol{x}') | \boldsymbol{\kappa}', \beta'; \boldsymbol{\kappa}, \beta \rangle \langle \boldsymbol{\kappa}', \beta'; \boldsymbol{\kappa}, \beta | \boldsymbol{A}(\boldsymbol{x}) | \boldsymbol{k}, \alpha \rangle \\
&\simeq \frac{\hbar\mu_0 c}{8\pi^3} \delta_{\alpha\alpha'} \delta(\boldsymbol{k}-\boldsymbol{k}') \int d^3\boldsymbol{\kappa} \sum_{\beta} \frac{\boldsymbol{\epsilon}_\beta(\boldsymbol{\kappa}) \otimes \boldsymbol{\epsilon}_\beta(\boldsymbol{\kappa})}{\kappa} \exp[\mathrm{i}c(\kappa+k)(t'-t)] \\
&\quad + \frac{\hbar\mu_0 c}{8\pi^3} \frac{\boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \otimes \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')}{\sqrt{kk'}} \exp[\mathrm{i}c(k+k')(t'-t)] \,. \qquad (18.71)
\end{aligned}$$

The first term in (18.71) corresponds to an electron self-energy contribution where the external photon does not interact with the electron, but there are two photons in the intermediate state due to emission and re-absorption of a virtual photon by the electron, see Fig. 18.1.

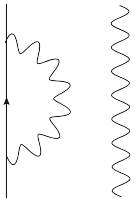


Figure 18.1: A process with two photons in an intermediate state due to emission and re-absorption of a virtual photon. The straight line represents the electron and the wavy lines represent photons.

This is an effect which leads to a renormalization of the electron mass in quantum field theory, but does not contribute to photon scattering.
The second term yields an expression for $S^{(I),2}$ which looks almost exactly like $S^{(I),0}$ (18.69), *except* that the polarization vectors are swapped $\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \leftrightarrow \boldsymbol{\epsilon}_\alpha(\boldsymbol{k})$, and $\omega_{n'',n} - ck - \mathrm{i}\epsilon$ is replaced by $\omega_{n'',n} + ck' - \mathrm{i}\epsilon$ in the denominator. After transformation into the length form, $S^{(I),0}$ and $S^{(I),2}$ yield the following expression,

$$\begin{aligned}
S^{(I)}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} &= \frac{\mu_0 c e^2}{8\pi^2 \mathrm{i}\hbar\sqrt{kk'}} \delta(\omega_{n',n} + \omega_{k',k}) \sum\!\!\!\!\!\!\int_{n'',\zeta''} \omega_{n',n''} \omega_{n'',n} \\
&\quad \times \left(\frac{\langle n', \zeta' | \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \mathbf{x} | n'', \zeta'' \rangle \langle n'', \zeta'' | \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \cdot \mathbf{x} | n, \zeta \rangle}{\omega_{n'',n} - ck - \mathrm{i}\epsilon} \right. \\
&\quad \left. + \frac{\langle n', \zeta' | \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \cdot \mathbf{x} | n'', \zeta'' \rangle \langle n'', \zeta'' | \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \mathbf{x} | n, \zeta \rangle}{\omega_{n'',n} + ck' - \mathrm{i}\epsilon} \right) . \qquad (18.72)
\end{aligned}$$

The first term corresponds to absorption of the initial photon before emission of the final photon, whereas the second term corresponds to emission of the final photon before absorption of the initial photon, see Fig. 18.2.

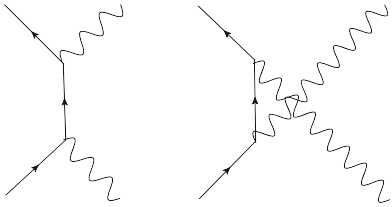


Figure 18.2: The left diagram corresponds to absorption of the initial photon before emission of the final photon. The diagram on the right hand side corresponds to emission of the final photon before absorption of the initial photon.

We separate the energy conserving δ function for the calculation of the scattering cross section,

$$S_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha} = -\mathrm{i}\mathcal{M}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\delta(\omega_{n',n}+\omega_{k',k}). \tag{18.73}$$

The differential scattering rate per $\boldsymbol{k}$ space volume of incident photons is then

$$\begin{aligned}\frac{d\Gamma_{n,\zeta;\boldsymbol{k},\alpha\to n',\zeta';\boldsymbol{k}',\alpha'}}{d^3\boldsymbol{k}} &= d^3\boldsymbol{k}'\frac{\left|S_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\right|^2}{T}\\ &= \frac{d^3\boldsymbol{k}'}{2\pi}\left|\mathcal{M}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\right|^2\delta(\omega_{n',n}+\omega_{k',k}),\end{aligned}$$

and the differential scattering cross section for polarized photons is with the incident photon current density per $\boldsymbol{k}$ space volume $d\boldsymbol{j}/d^3\boldsymbol{k} = c\hat{\boldsymbol{k}}/(2\pi)^3$ (18.61),

$$\begin{aligned}d\sigma_{n,\zeta;\boldsymbol{k},\alpha\to n',\zeta';\boldsymbol{k}',\alpha'} &= \frac{d\Gamma_{n,\zeta;\boldsymbol{k},\alpha\to n',\zeta';\boldsymbol{k}',\alpha'}}{dj(\boldsymbol{k})}\\ &= \frac{4\pi^2}{c}\left|\mathcal{M}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\right|^2\delta(\omega_{n',n}+\omega_{k',k})d^3\boldsymbol{k}'.\end{aligned} \tag{18.74}$$

This yields after integration over k'

$$\frac{d\sigma_{n,\zeta;\boldsymbol{k},\alpha\to n',\zeta';\boldsymbol{k}',\alpha'}}{d\Omega} = \frac{4\pi^2}{c^2}k'^2\left|\mathcal{M}_{n',\zeta';\boldsymbol{k}',\alpha'|n,\zeta;\boldsymbol{k},\alpha}\right|^2\Big|_{k'=k-(\omega_{n',n}/c)}. \tag{18.75}$$

Substitution of our results for $S^{(I)}$ and $S^{(II)}$ yields for the differential scattering cross section $d\sigma_{n,\zeta;\boldsymbol{k},\alpha\to n',\zeta';\boldsymbol{k}',\alpha'}/d\Omega$ the result

$$\begin{aligned}\frac{d\sigma}{d\Omega} = \left(\frac{\mu_0 e^2}{4\pi}\right)^2\frac{k'}{k}\Bigg|&\frac{1}{m}\delta_{n'n}\delta_{\zeta'\zeta}\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) + \sum\!\!\!\!\!\!\int_{n'',\zeta''}\omega_{n',n''}\omega_{n'',n}\\ &\times\Bigg(\frac{\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n'',\zeta''\rangle\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n,\zeta\rangle}{\hbar\omega_{n'',n}-\hbar ck-\mathrm{i}\epsilon}\\ &+\frac{\langle n',\zeta'|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|n'',\zeta''\rangle\langle n'',\zeta''|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n,\zeta\rangle}{\hbar\omega_{n'',n}+\hbar ck'-\mathrm{i}\epsilon}\Bigg)\Bigg|^2_{k'=k-(\omega_{n',n}/c)}\end{aligned} \tag{18.76}$$

If there are non-vanishing transition matrix elements $\langle n', \zeta' | \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \mathbf{x} | n'', \zeta'' \rangle$ and $\langle n'', \zeta'' | \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) \cdot \mathbf{x} | n, \zeta \rangle$ with the properties $\omega_{n'',n} \simeq ck$ and $\omega_{n',n''} \simeq -ck'$, or if there are any non-vanishing matrix elements $\langle n', \zeta' | \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) \cdot \mathbf{x} | n'', \zeta'' \rangle$ and $\langle n'', \zeta'' | \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \mathbf{x} | n, \zeta \rangle$ with the properties $\omega_{n'',n} \simeq -ck'$ and $\omega_{n',n''} \simeq ck$, then the differential scattering cross section will be dominated by the resonantly enhanced contributions from those matrix elements, and we will have $\omega_{n',n''}\omega_{n'',n} \simeq -c^2kk'$ for the dominant terms. In these cases we can approximate our result (18.76) by the equation

$$\begin{aligned}\frac{d\sigma}{d\Omega} \simeq & \left(\frac{e^2}{4\pi\epsilon_0\hbar}\right)^2 kk'^3 \\ & \times \left| \sum\!\!\!\!\!\!\int_{n'',\zeta''} \left(\frac{\langle n', \zeta' | \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \mathbf{x} | n'', \zeta'' \rangle \langle n'', \zeta'' | \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) \cdot \mathbf{x} | n, \zeta \rangle}{\omega_{n'',n} - ck - \mathrm{i}\epsilon} \right.\right. \\ & \left.\left. + \frac{\langle n', \zeta' | \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) \cdot \mathbf{x} | n'', \zeta'' \rangle \langle n'', \zeta'' | \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \mathbf{x} | n, \zeta \rangle}{\omega_{n'',n} + ck' - \mathrm{i}\epsilon} \right) \right|^2_{k'=k-(\omega_{n',n}/c)} \end{aligned} \tag{18.77}$$

This is an equation for photon scattering which was proposed already in 1924 by Kramers and Heisenberg based on the correspondence principle[5]. However, note that this is only a suitable approximation to the actual cross section (18.76) if the near resonance conditions $\omega_{n'',n} \simeq ck$ and $\omega_{n',n''} \simeq -ck'$, or $\omega_{n'',n} \simeq -ck'$ and $\omega_{n',n''} \simeq ck$, can be fulfilled, and if there are allowed dipole transitions into the intermediate nearly resonant levels.

Thomson cross section

The contribution from the first term in (18.76) coincides with the classical Thomson cross section for elastic scattering of light which we will encounter again in Section 21.7 when we discuss photon scattering off free electrons. The first term yields for scattering of polarized photons

$$\left.\frac{d\sigma_T}{d\Omega}\right|_{\alpha\to\alpha'} = \left(\frac{\mu_0 e^2}{4\pi m}\right)^2 (\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}))^2 = \left(\frac{\mu_0 e^2}{4\pi m}\right)^2 \cos^2\theta_{\alpha\alpha'},$$

The resulting cross section for unpolarized light involves a sum over final polarizations and an average over initial polarizations,

$$\begin{aligned} & \frac{1}{2}\sum_{\alpha,\alpha'} \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) \otimes \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) \cdot \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \\ & = \frac{1}{2}\sum_{\alpha'} \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \left(\underline{1} - \hat{\boldsymbol{k}} \otimes \hat{\boldsymbol{k}}\right) \cdot \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \\ & = \frac{1}{2}\mathrm{tr}\left[\left(\underline{1} - \hat{\boldsymbol{k}} \otimes \hat{\boldsymbol{k}}\right) \cdot \left(\underline{1} - \hat{\boldsymbol{k}}' \otimes \hat{\boldsymbol{k}}'\right)\right] = \frac{1+\cos^2\theta}{2}, \end{aligned} \tag{18.78}$$

[5] H.A. Kramers & W. Heisenberg, Z. Phys. 31, 681 (1925).

where $\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{k}}' = \cos\theta$, i.e. θ is the scattering angle. This yields[6]

$$\frac{d\sigma_T}{d\Omega} = \left(\frac{\mu_0 e^2}{4\pi m}\right)^2 \frac{1+\cos^2\theta}{2}, \tag{18.79}$$

and

$$\sigma_T = \frac{8\pi}{3}\left(\frac{\mu_0 e^2}{4\pi m}\right)^2. \tag{18.80}$$

The first term in equation (18.76) would hypothetically dominate the cross section $d\sigma/d\Omega$ if the photon energy is much larger than all the excitation energies of dipole allowed transitions, i.e. if $ck \gg |\omega_{n'',n}|$ for all $\langle n'', \zeta''|\mathbf{x}|n, \zeta\rangle \neq 0$. However, there will always be allowed transitions into intermediate continuum states. Therefore the condition $ck \gg |\omega_{n'',n}|$ for all dipole allowed transitions will not be fulfilled and the first term in (18.76) will never dominate light scattering by atoms or molecules[7]. However, the Thomson cross section plays an important role in the scattering of light by free electrons, which will be discussed in Section 21.7.

Rayleigh scattering

Molecules in a gas or a liquid have many dense lying rotational and vibrational levels, and the condition of dipole allowed resonant excitation of intermediate levels will practically always be fulfilled. The Kramers-Heisenberg formula (18.77) will therefore always be an excellent approximation to (18.76) for molecules in a fluid phase. In particular, the cross section for elastic photon scattering $|g; \boldsymbol{k}, \alpha\rangle \to |g; \boldsymbol{k}', \alpha'\rangle$ from a ground state $|g\rangle$ or a state $|g\rangle$ near the ground state will be

$$\frac{d\sigma_R}{d\Omega} \simeq \left(\frac{e^2k^2}{4\pi\epsilon_0\hbar}\right)^2 \left| \sum_{n,\zeta,\omega_{n,g}\simeq ck} \frac{\langle g|\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}')\cdot\mathbf{x}|n,\zeta\rangle\langle n,\zeta|\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\cdot\mathbf{x}|g\rangle}{\omega_{n,g} - ck - \mathrm{i}\epsilon} \right|^2. \tag{18.81}$$

A formula for resonance fluorescence which is equivalent to (18.81) was given for the first time by Viktor Weisskopf in his Ph.D. thesis[8].

The reasoning with only one kind of resonantly enhanced terms is correct as long as the alternative resonance condition $\omega_{n,g} \simeq -ck$ cannot be fulfilled, i.e. as long as the energy E_g of the initial state $|g\rangle$ is less than $\hbar ck$ above the ground state energy. This applies e.g. to molecules at room temperature. These molecules will generically occupy states with energies less than 0.1 eV above

[6] The combination $r_e \equiv \mu_0 e^2/4\pi m = 2.82\,\mathrm{fm}$ is also denoted as the *classical radius of the electron.*

[7] A loophole in this argument concerns the remote possibility that all the matrix elements $\langle n'', \zeta''|\mathbf{x}|n, \zeta\rangle$ with $\omega_{n'',n} \gtrsim ck$ are extremely small.

[8] V. Weisskopf, Annalen Phys. 401, 23 (1931). He used a dipole operator $H = -e\boldsymbol{x}\cdot\dot{\boldsymbol{A}}(\boldsymbol{x}, t)$ for atom-photon interactions throughout his calculations.

their ground state energy. Scattering of optical photons by these molecules can be described by equation (18.81).
We can connect (18.81) to the polarizability properties of the scattering centers by noting that the dynamical polarizability tensor (15.22) for $\omega_{mn} \simeq \omega = ck$ has exactly the same form as the tensor multiplying the polarization vectors in (18.81). Therefore we can rewrite this equation also in the form

$$\left.\frac{d\sigma_R}{d\Omega}\right|_{\alpha\to\alpha'} = \left(\frac{\mu_0}{4\pi}\right)^2 \omega^4 \left(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \underline{\alpha}_{(g)} \cdot \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k})\right)^2, \tag{18.82}$$

where it is understood that the sum over intermediate levels in (15.22) is dominated by terms which are almost resonant with the frequency ω of the elastically scattered photons.
Directional averaging over the orientation of the molecules will lead to an isotropic effective polarization tensor,

$$\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \underline{\alpha}_{(g)} \cdot \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}) = \alpha_{(g)} \boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{k}') \cdot \boldsymbol{\epsilon}_{\alpha}(\boldsymbol{k}),$$

$$\left.\frac{d\sigma_R}{d\Omega}\right|_{\alpha\to\alpha'} = \left(\frac{\mu_0}{4\pi}\alpha_{(g)}\right)^2 \omega^4 \cos^2\theta_{\alpha\alpha'},$$

and averaging and summation over the polarizations of the incoming and scattered photons (18.78) yields the same angular dependence on the scattering angle as for Thomson scattering (18.79),

$$\frac{d\sigma_R}{d\Omega} = \left(\frac{\mu_0}{4\pi}\alpha_{(g)}\right)^2 \omega^4 \frac{1+\cos^2\theta}{2} \tag{18.83}$$

and

$$\sigma_R = \frac{8\pi}{3}\left(\frac{\mu_0}{4\pi}\alpha_{(g)}\right)^2 \omega^4. \tag{18.84}$$

Equations (18.83,18.84) are quantum mechanical versions of Lord Rayleigh's ω^4 law (Rayleigh 1871, 1899; see also Jackson [17] for a derivation of Rayleigh scattering in classical electrodynamics). It is sometimes stated (but neither in [17] nor in Weisskopf's thesis) that Rayleigh scattering is a small frequency approximation in the sense that $\hbar\omega = \hbar ck$ should be small compared to the internal excitations of the scattering system. This is not true. The quantum mechanical derivation (as well as Jackson's classical derivation) does not require this assumption. The only assumption that went into our derivation above was resonantly enhanced dipole scattering. Besides, energies of optical photons are not small compared to excitation energies for nitrogen or oxygen molecules. Indeed, the assumption of resonantly enhanced dipole scattering implies that the photon frequency $\omega = ck$ should be comparable to the transition frequencies of some dipole allowed transitions.

18.9 Problems

18.1 Prove that the vector field (18.14) satisfies $\boldsymbol{\nabla} \cdot \boldsymbol{A}_J(\boldsymbol{x}, t) = 0$.

18.2 Show that in the gauge $\Phi = 0$ the conjugate momentum $\boldsymbol{\Pi}_{\boldsymbol{A}} = \partial \mathcal{L} / \partial \dot{\boldsymbol{A}} = \epsilon_0 \dot{\boldsymbol{A}}$ also yields the Hamiltonian density $\mathcal{H}$ through the standard Lagrangian expression

$$\mathcal{H} = \boldsymbol{\Pi}_{\boldsymbol{A}} \cdot \dot{\boldsymbol{A}} - \mathcal{L} = \epsilon_0 \dot{\boldsymbol{A}}^2 - \mathcal{L}.$$

18.3 A helium-neon laser produces a light wave with a central wavelength of 632.8 nm and a power of 5 mW. Suppose the electric component is a sinus oscillation $|\boldsymbol{E}(\boldsymbol{x}, t)| \propto \sin(\boldsymbol{k} \cdot \boldsymbol{x} - ckt)$ and is polarized in x direction. We also assume that the frequency profile is Gaussian with a relative width $\Delta f / f = 3.16 \times 10^{-6}$. Which photon state describes this light wave? How many photons does the electromagnetic wave contain?

18.4 Calculate the emission rate for unpolarized photons from the 2p state to the ground state of hydrogen in first order and dipole approximation.
Which estimate do you get from this for the lifetime of 2p states?
Which estimate do you get from this for the radiated power from decay of 2p states?

18.5 Calculate the integrated photon absorption cross section,

$$G_{1s \to 2p} = \int_0^\infty \frac{dk}{k} \, \sigma_{1,0 \to 2,1}(k)$$

due to the transition from 1s to 2p states in hydrogen.

18.6a Show that the first order scattering matrix elements (18.41) and (18.55) for emission and absorption can also be gotten in a semi-classical approximation from a perturbation operator

$$V(t) = -q\mathbf{x} \cdot \boldsymbol{E}(\mathbf{x}, t) \tag{18.85}$$

with $\boldsymbol{E}(\mathbf{x}, t)$ corresponding to a single photon electric field

$$\boldsymbol{E}_\alpha^{(+)}(\boldsymbol{x}, t) = -\dot{\boldsymbol{A}}_\alpha^{(+)}(\boldsymbol{x}, t) = -\mathrm{i}\sqrt{\frac{\hbar \mu_0 c^3 k}{16\pi^3}} \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \exp[-\mathrm{i}(\boldsymbol{k} \cdot \boldsymbol{x} - ckt)]$$

for emission, and to

$$\boldsymbol{E}_\alpha^{(-)}(\boldsymbol{x}, t) = -\dot{\boldsymbol{A}}_\alpha^{(-)}(\boldsymbol{x}, t) = \mathrm{i}\sqrt{\frac{\hbar \mu_0 c^3 k}{16\pi^3}} \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}) \exp[\mathrm{i}(\boldsymbol{k} \cdot \boldsymbol{x} - ckt)]$$

for absorption.

18.6b If we would use the same substitution of semi-classical perturbation operators $V(t)$ from (18.42) to (18.85) for the calculation of scattering in dipole approximation $\exp(\pm \mathrm{i}\boldsymbol{k} \cdot \boldsymbol{x}) \simeq 1$, we would find the Kramers-Heisenberg formula (18.77) from (18.85), while (18.42) yields the correct result (18.76). Why

does the substitution (18.42) → (18.85) not work beyond first order perturbation theory, except in the case of resonances?
Hint: The justification for the transition from the velocity form to the length form of matrix elements is based on

$$\frac{\mathbf{p}}{m} = \frac{\mathrm{i}}{\hbar}[H, \mathbf{x}] \;\Rightarrow\; \langle f|\frac{\mathbf{p}}{m}|i\rangle = \mathrm{i}\omega_{fi}\langle f|\mathbf{x}|i\rangle.$$

18.7 Ultraviolet photons with an energy $E_\gamma = 10.15$ eV are nearly resonant with the $n = 1 \to n'' = 2$ transition in hydrogen. Use both the result (18.76) and the Kramers-Heisenberg formula (18.77) to estimate the differential scattering cross section for a photon scattering angle of $\pi/2$ if the incident photons are polarized in z direction and move in x direction. Assume that the scattered photons move in y direction with polarization $\boldsymbol{e}_z \cos\alpha + \boldsymbol{e}_x \sin\alpha$.

Chapter 19

Quantum Aspects of Materials II

We have already seen in Chapter 10 that basic properties of electron states in materials are determined by quantum effects. This impacts all properties of materials, including their mechanical properties, electrical and thermal conductivities, and optical properties. An example of the inherently quantum mechanical nature of electrical properties is provided by the role of virtual intermediate states in the polarizability tensor in Section 15.3.

We will now continue to illustrate quantum effects in materials with a focus on effects that require the use of second quantization or Lagrangian field theory, or at least the knowledge of exchange interactions for a proper treatment. We will start at the molecular level and then discuss the second quantization of basic excitations in condensed materials.

The inception of the Schrödinger equation was accompanied by a large number of immediate successes, including atomic theory, the quantum theory of photon-atom interactions, and quantum tunneling. Another of these important successes was the development of the theory of covalent chemical bonding, which was initiated by by Burrau[1], Heitler and London[2], and others. This is an extremely important and well studied subject in chemistry and molecular physics, and yet it never seemed to reach the level of popularity and recognition that other areas of applied quantum mechanics enjoy. One reason for this lack of popularity might be the lack of simple, beautiful model systems which can be solved analytically. Solvable model systems are of great instructive and illustrative value, and often provide a level of insight that is very hard to attain with systems which can only be analyzed by approximation methods. However, the existence and stability of covalent bonds is clearly an important property of molecules and of materials in general, and a basic quantitative understanding of the covalent bond should be part of the toolbox of every chemist, physicist and materials scientist. Indeed, there is a model system which can be analyzed

[1] Ø. Burrau, Naturwissenschaften 15, 16 (1927); K. Danske Vidensk. Selsk., Mat.-fys. Medd. 7(14) (1927).

[2] W. Heitler & F. London, Z. Phys. 44, 455 (1927).

R. Dick, *Advanced Quantum Mechanics: Materials and Photons*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-8077-9_19,
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to some extent by analytic methods. If only basic qualitative features are required, the analytic formulation can then be used for numerical evaluations which do not require a huge amount of effort. This model system is the hydrogen molecule ion H_2^+, which is also known as the dihydrogen cation. The analysis of electron states for fixed locations of the two protons in this simplest molecular system have been investigated already in the early years of quantum mechanics[3], and have been a subject of research ever since, both in terms of the semi-analytic analysis in prolate spheroidal coordinates[4] used in Section 19.2, and in terms of high precision variational calculations[5]. Before specializing to H_2^+ we will discuss the interplay of nuclear and electronic coordinates and the role of the Born-Oppenheimer approximation in molecular physics.

19.1 The Born-Oppenheimer approximation

Molecules can be described by first quantized Hamiltonians of the form

$$H = \sum_i \frac{\boldsymbol{p}_i^2}{2m_e} + \sum_I \frac{\boldsymbol{P}_I^2}{2M_I} + \sum_{I<J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |\boldsymbol{R}_I - \boldsymbol{R}_J|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i,J} \frac{Z_J e^2}{4\pi\epsilon_0 |\boldsymbol{r}_i - \boldsymbol{R}_J|} \tag{19.1}$$

if we use properly anti-symmetrized wave functions for the electrons and symmetrized or anti-symmetrized wave functions for bosonic or fermionic nuclei of the same kind. Here lower case indices enumerate electrons while upper case indices refer to nuclei.
Otherwise, we might just as well use the second quantized Schrödinger picture Hamiltonian

$$\begin{aligned} H = & \int d^3\boldsymbol{x} \left(\frac{\hbar^2}{2m_e} \boldsymbol{\nabla}\psi_e^+(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\psi_e(\boldsymbol{x}) + \sum_A \frac{\hbar^2}{2M_A} \boldsymbol{\nabla}\psi_A^+(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\psi_A(\boldsymbol{x}) \right) \\ & + \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \frac{e^2}{4\pi\epsilon_0 |\boldsymbol{x} - \boldsymbol{x}'|} \left(\sum_{A<B} Z_A Z_B \psi_A^+(\boldsymbol{x}) \psi_B^+(\boldsymbol{x}') \psi_B(\boldsymbol{x}') \psi_A(\boldsymbol{x}) \right. \\ & + \sum_A \frac{Z_A}{2} \psi_A^+(\boldsymbol{x}) \psi_A^+(\boldsymbol{x}') \psi_A(\boldsymbol{x}') \psi_A(\boldsymbol{x}) + \frac{1}{2} \psi_e^+(\boldsymbol{x}) \psi_e^+(\boldsymbol{x}') \psi_e(\boldsymbol{x}') \psi_e(\boldsymbol{x}) \\ & \left. - \sum_A Z_A \psi_e^+(\boldsymbol{x}) \psi_A^+(\boldsymbol{x}') \psi_A(\boldsymbol{x}') \psi_e(\boldsymbol{x}) \right), \end{aligned} \tag{19.2}$$

[3] A.H. Wilson, Proc. Roy. Soc. London A 118, 617, 635 (1928); E. Teller, Z. Phys. 61, 458 (1930); E.A. Hylleraas, Z. Phys. 71, 739 (1931); G. Jaffé, Z. Phys. 87, 535 (1934).

[4] See e.g. G. Hunter & H.O. Pritchard, J. Chem. Phys. 46, 2146 (1967); M. Aubert, N. Bessis & G. Bessis, Phys. Rev. A 10, 51 (1974); T.C. Scott, M. Aubert-Frécon & J. Grotendorf, Chem. Phys. 324, 323 (2006).

[5] B. Grémaud, D. Delande & N. Billy, J. Phys. B 31, 383 (1998); M.M. Cassar & G.W.F. Drake, J. Phys. B 37, 2485 (2004); H. Li, J. Wu, B.-L. Zhou, J.-M. Zhu & Z.-C. Yan, Phys. Rev. A 75, 012504 (2007).

where the labels A, B enumerate different kinds of nuclei. We assume that there are N_e electrons and $N_n = \sum_A N_A$ nuclei in our molecule. Realistically, we would restrict attention to valence electrons (rather than all electrons), and the numbers A would enumerate different kinds of ion cores. However, in the example of the hydrogen molecule ion below this distinction is void.
Spin labels are suppressed in (19.2) and also in the corresponding states below, because they enter trivially in the equations of motion[6].
Note that even in the valence electrons plus ion cores approximation, the Hamiltonians (19.1,19.2) describe an incredibly complicated quantum mechanical system, even in the case of a "simple" diatomic molecule. This is because the complete spectrum of energy levels and eigenstates of (19.1) does not only include bound molecular states (which is complicated enough), but also scattering states of electrons and of molecular fragments. The Hamiltonian for the hydrogen molecule H_2 describes not only bound states of two protons and two electrons, but also electron scattering off an H_2^+ ion, atomic hydrogen-hydrogen scattering, proton scattering off an H^- ion, and a plasma of free protons and electrons. However, our primary interest concerns an understanding of the nature of covalent bonds and of ground state properties of molecules. In this case, we don't have to include the scattering states, and we can even neglect the motion of ion cores.
Born and Oppenheimer have pointed out that it makes intuitive sense to separate nuclear and electronic motion by first solving the electronic problem for fixed nuclear coordinates, and then substituting the electronic solution into a remnant nuclear Schrödinger equation[7]. In the framework of quantized Schrödinger theory this amounts to an electronic Hamiltonian

$$H_e = H - \int d^3\boldsymbol{x} \sum_A \frac{\hbar^2}{2M_A} \boldsymbol{\nabla}\psi_A^+(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\psi_A(\boldsymbol{x}) \tag{19.3}$$

with corresponding parameter dependent electronic states

$$\begin{aligned} |\boldsymbol{n}; \boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n}\rangle = \prod_{i=1}^{N_e} \int d^3\boldsymbol{x}_i \, \psi_e^+(\boldsymbol{x}_i) \prod_{I=1}^{N_n} \psi_{A(I)}^+(\boldsymbol{X}_I)|0\rangle \\ \times \langle \boldsymbol{x}_1, \ldots \boldsymbol{x}_{N_e}|\boldsymbol{n}; \boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n}\rangle. \end{aligned} \tag{19.4}$$

Here $\psi_e^+(\boldsymbol{x}_i)$ is an electronic creation operator and $\psi_{A(I)}^+(\boldsymbol{X}_I)$ is a creation operator for a nucleus of species A at the location $\boldsymbol{X}_I$. The set of quantum numbers $\boldsymbol{n}$ specifies the state (including the energy level), and the notation $|\boldsymbol{n}; \boldsymbol{X}_1, \ldots \boldsymbol{X}_{N_n}\rangle$ indicates that the electronic state also depends on the location of the nuclei.
The equation of motion for the electronic states (19.4) with the Hamiltonian (19.3) then follows as in Section 17.6, except that here we use a

[6] We would have to be more careful if we would discuss expectation values, because exchange integrals appear in the expectation values of potential terms, see Section 17.7.
[7] M. Born & J.R. Oppenheimer, Annalen Phys. 84, 457 (1927).

time-independent Schrödinger equation. The equation

$$E_{e,\boldsymbol{n}}(\boldsymbol{X}_1,\dots\boldsymbol{X}_{N_n})|\boldsymbol{n};\boldsymbol{X}_1,\dots\boldsymbol{X}_{N_n}\rangle = H_e|\boldsymbol{n};\boldsymbol{X}_1,\dots\boldsymbol{X}_{N_n}\rangle$$

yields with the short hand notation $\langle\boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle \equiv \langle\boldsymbol{x}_1,\dots\boldsymbol{x}_{N_e}|\boldsymbol{n};\boldsymbol{X}_1,\dots\boldsymbol{X}_{N_n}\rangle$ the equation

$$\begin{aligned} E_{e,\boldsymbol{n}}(\boldsymbol{X})\langle\boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle = &-\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial\boldsymbol{x}_i^2}\langle\boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle. \\ &+\frac{e^2}{4\pi\epsilon_0}\left(\sum_{i<j}\frac{1}{|\boldsymbol{x}_i-\boldsymbol{x}_j|}-\sum_{i,I}\frac{Z_{A(I)}}{|\boldsymbol{x}_i-\boldsymbol{X}_I|}\right. \\ &\left.+\sum_{I<J}\frac{Z_{A(I)}Z_{A(J)}}{|\boldsymbol{X}_I-\boldsymbol{X}_J|}\right)\langle\boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle \end{aligned} \tag{19.5}$$

The N_e-electron wave functions $\langle\boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle$ are complete in the $3N_e$-dimensional configuration space of the electrons, and therefore the wave functions of the full (N_e+N_n)-particle problem can be expanded in the form

$$\langle\boldsymbol{x},\boldsymbol{X}|E\rangle = \sum_{\boldsymbol{n}} c(\boldsymbol{n};\boldsymbol{X})\langle\boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle. \tag{19.6}$$

The sum over the quantum numbers $\boldsymbol{n}$ also involves at least one integration over a continuous quantum number for the scattering states.
On the level of the second quantized theory, the amplitude (19.6) corresponds to the (N_e+N_n)-particle state

$$\begin{aligned} |E\rangle &= \prod_{i=1}^{N_e}\int d^3\boldsymbol{x}_i\,\psi_e^+(\boldsymbol{x}_i)\prod_{I=1}^{N_n}\int d^3\boldsymbol{X}_I\,\psi_{A(I)}^+(\boldsymbol{X}_I)|0\rangle\langle\boldsymbol{x},\boldsymbol{X}|E\rangle \\ &= \prod_{I=1}^{N_n}\int d^3\boldsymbol{X}_I\sum_{\boldsymbol{n}} c(\boldsymbol{n};\boldsymbol{X})|\boldsymbol{n};\boldsymbol{X})\rangle, \end{aligned}$$

where the parameter-dependent electronic state $|\boldsymbol{n};\boldsymbol{X})\rangle$ is given in (19.4). Substituting (19.6) into the full (N_e+N_n)-particle Schrödinger equation

$$H|E\rangle = E|E\rangle$$

yields the equation

$$\sum_{\boldsymbol{n}}\left(\sum_{I=1}^{N_n}\frac{\hbar^2}{2M_{A(I)}}\frac{\partial^2}{\partial\boldsymbol{X}_I^2} - E_{e,\boldsymbol{n}}(\boldsymbol{X}) + E\right)c(\boldsymbol{n};\boldsymbol{X})\langle\boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle = 0. \tag{19.7}$$

This can be resolved into a set of coupled equations for the nuclear factors $c(\boldsymbol{n};\boldsymbol{X})$ through orthogonality of the electron factors $\langle\boldsymbol{x}|\boldsymbol{n};\boldsymbol{X}\rangle$. If this is done, no approximation has been made so far to the problem to solve the molecular Hamiltonian (19.2). However, if we are in the center of mass frame of the nuclei,

and if both rotational and vibrational excitations are small, we can neglect the nuclear kinetic terms, and we find for these nuclear configurations $\boldsymbol{X}^{(0)}$ that their energy levels can be approximated by

$$E = E_{e,\boldsymbol{n}}(\boldsymbol{X}^{(0)}). \tag{19.8}$$

The corresponding full molecular eigenstate in this approximation is

$$\langle \boldsymbol{x}, \boldsymbol{X} | E_{e,\boldsymbol{n}}(\boldsymbol{X}^{(0)})\rangle = \delta(\boldsymbol{X} - \boldsymbol{X}^{(0)})\langle \boldsymbol{x}|\boldsymbol{n}; \boldsymbol{X}^{(0)}\rangle, \tag{19.9}$$

$$\begin{aligned} |E_{e,\boldsymbol{n}}(\boldsymbol{X}^{(0)})\rangle = \prod_{i=1}^{N_e} \int d^3\boldsymbol{x}_i\, \psi_e^+(\boldsymbol{x}_i) \prod_{I=1}^{N_n} \int d^3\boldsymbol{X}_I\, \psi_{A(I)}^+(\boldsymbol{X}_I)|0\rangle \\ \times \langle \boldsymbol{x}, \boldsymbol{X}|E_{e,\boldsymbol{n}}(\boldsymbol{X}^{(0)})\rangle = |\boldsymbol{n}; \boldsymbol{X}^{(0)}\rangle. \end{aligned}$$

It might be tempting to conclude from (19.8) that the solution of the electronic equation (19.5) eventually allows us to calculate the nuclear equilibrium configuration $\boldsymbol{X}^{(0)}$ in the aftermath from a requirement $[\partial E_{e,\boldsymbol{n}}(\boldsymbol{X})/\partial \boldsymbol{X}]_{\boldsymbol{X}=\boldsymbol{X}^{(0)}} = 0$. However, *this is not true*: *The energy level $E_{e,\boldsymbol{n}}(\boldsymbol{X})$ for a general nuclear configuration $\boldsymbol{X}$ represents only the electronic energy plus the electrostatic nuclear potential energy for that configuration.* Equation (19.8) only states that within the Born-Oppenheimer approximation, the energy $E_{e,\boldsymbol{n}}(\boldsymbol{X})$ and the full molecular energy coincide in an equilibrium configuration, but that does *not* imply that the two energies coincide in a *neighborhood* of an equilibrium configuration. As a consequence the energy $E_{e,\boldsymbol{n}}(\boldsymbol{X})$ and the full molecular energy can (and generically will) have *different gradients* with respect to the nuclear configuration, even in a molecular equilibrium configuration. The function $E_{e,\boldsymbol{n}}(\boldsymbol{X})$ may have non-vanishing gradient in the molecular equilibrium configuration because it neglects the contributions from nuclear kinetic terms. Therefore we have to use *a priori* knowledge of the equilibrium configuration $\boldsymbol{X}^{(0)}$, e.g. from scattering experiments, to calculate the molecular energy in the Born-Oppenheimer approximation. We *cannot calculate both* the energy and the equilibrium configuration from (19.5).

19.2 Covalent bonding – the hydrogen molecule ion

The stability of molecules is an issue in classical physics in the same sense as the stability of atoms is an issue. It is not surprising that sharing of electrons yields a net attractive force between positively charged nuclei or atomic cores. Consider e.g. two protons at separation b with an electron right in the middle between the protons. The net classical electrostatic energy of the system $\propto -3e^2/b$ is attractive, but the problem is again to prevent collapse of the system. The corresponding quantum mechanical system is again stabilized by wave particle duality. Squeezing the particles very tight together implies strongly

peaked wave functions, hence too much curvature in the wave functions, and the ensuing increase in kinetic energy eventually cannot be compensated any more by gains in potential energy terms for normalizable wave functions.
We apply the basic tenet of the Born-Oppenheimer approximation to the hydrogen molecule ion H_2^+ and determine approximate molecular orbitals under the assumption that the two protons are fixed at their equilibrium separation b. The distances of the electron from the two protons are given by

$$r_\pm^2 = x^2 + y^2 + (z \pm (b/2))^2 \tag{19.10}$$

if we assume that the two protons are located on the z axis at $z = \pm b/2$. A suitable set of coordinates for the 2-center Coulomb problem are given by

$$\xi^+ = r_+ + r_-, \quad b \leq \xi^+,$$

$$\xi^- = r_+ - r_-, \quad -b \leq \xi^- \leq b$$

and the azimuthal angle φ around the z axis. These coordinates are known as prolate spheroidal coordinates. They seem to have been used for the analysis of classical 2-center gravitational or electrostatic problems and for acoustic and electromagnetic radiation problems since the 19th century.
The surfaces $\xi^+ = const.$ are ellipsoids with the protons in the focal points, while the surfaces $\xi^- = const.$ are the corresponding hyperboloids. The ξ^- coordinate lines take us from one hyperboloid $\xi^- = const.$ to another hyperboloid $\xi^- = const.$ for constant ξ^+ and φ. For given value of ξ^+, going from $\xi^- = -b$ to $\xi^- = b$ takes us from the south pole of the ellipsoid $\xi^+ = const.$ to its north pole, i.e. ξ^-/b is similar to the ϑ coordinate on a sphere, except that we move from negative z to positive z for increasing ξ^-. The advantage of this is that $z > 0$ corresponds to $\xi^- > 0$, but the right handed prolate spheroidal coordinate system is then $\{\xi^-, \xi^+, \varphi\}$.
The ξ^+ coordinate lines are hyperbolas $\xi^- = const.$, $\varphi = const.$ with the protons in the focal points. $\xi^+ = b$ corresponds to the line $-b/2 \leq z \leq b/2$ on the z axis and $\xi^+ \to \infty$ takes us to infinite distance from the protons, i.e. ξ^+ plays a role similar to the radius r in spherical coordinates.
We apply the methods of Section 5.4 to determine tangent vectors to the coordinate lines and the relevant differential operators. We have

$$2r^2 + \frac{b^2}{2} = r_+^2 + r_-^2 = \frac{1}{2}(\xi^+)^2 + \frac{1}{2}(\xi^-)^2$$

and

$$z = \frac{\xi^+\xi^-}{2b},$$

and this implies also

$$x^2 + y^2 = \frac{b^2(\xi^+)^2 + b^2(\xi^-)^2 - (\xi^+\xi^-)^2 - b^4}{4b^2} = \frac{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]}{4b^2},$$

$$x = \frac{1}{2b}\sqrt{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]}\cos\varphi,$$
$$y = \frac{1}{2b}\sqrt{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]}\sin\varphi.$$

The dual basis vectors (5.19) are in the present case

$$\boldsymbol{\nabla}\xi^+ = \frac{1}{2r_+r_-}\left(2\xi^+\boldsymbol{r} - b\xi^-\boldsymbol{e}_z\right), \quad \boldsymbol{\nabla}\xi^- = -\frac{1}{2r_+r_-}\left(2\xi^-\boldsymbol{r} - b\xi^+\boldsymbol{e}_z\right),$$

and

$$\boldsymbol{\nabla}\varphi = \frac{x\boldsymbol{e}_y - y\boldsymbol{e}_x}{x^2 + y^2}.$$

This yields a diagonal inverse metric with components

$$g^{++} = 4\frac{(\xi^+)^2 - b^2}{(\xi^+)^2 - (\xi^-)^2}, \quad g^{--} = 4\frac{b^2 - (\xi^-)^2}{(\xi^+)^2 - (\xi^-)^2},$$
$$g^{\varphi\varphi} = \frac{4b^2}{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]},$$

and the volume measure (5.25) for $d\xi^- d\xi^+ d\varphi$ follows as

$$\sqrt{g} = \left(g^{++}g^{--}g^{\varphi\varphi}\right)^{-1/2} = \frac{1}{8b}[(\xi^+)^2 - (\xi^-)^2]. \tag{19.11}$$

The Laplace operator (5.24) in spheroidal coordinates is therefore

$$\Delta = \frac{4}{(\xi^+)^2 - (\xi^-)^2}\left[\partial_+\left((\xi^+)^2 - b^2\right)\partial_+ + \partial_-\left(b^2 - (\xi^-)^2\right)\partial_-\right] + \frac{4b^2}{[(\xi^+)^2 - b^2][b^2 - (\xi^-)^2]}\partial_\varphi^2. \tag{19.12}$$

On the other hand, the coordinate dependence of the electrostatic potential of the electron is

$$\frac{1}{r_+} + \frac{1}{r_-} = \frac{4\xi^+}{(\xi^+)^2 - (\xi^-)^2},$$

and therefore the Hamiltonian in the $\{\xi^+, \xi^-, \varphi\}$ representation satisfies

$$\frac{m_e}{2\hbar^2}[(\xi^-)^2 - (\xi^+)^2]H = \partial_+\left((\xi^+)^2 - b^2\right)\partial_+ + \partial_-\left(b^2 - (\xi^-)^2\right)\partial_- + \left(\frac{b^2}{(\xi^+)^2 - b^2} + \frac{b^2}{b^2 - (\xi^-)^2}\right)\partial_\varphi^2 + \frac{m_e e^2}{2\pi\epsilon_0\hbar^2}\xi^+. \tag{19.13}$$

The Hamiltonian H commutes with the azimuthal angular momentum operator L_z, and therefore we can discuss the spectrum and eigenfunctions of H within the subspaces of L_z eigenvalues $m\hbar$,

$$\psi_m(\xi^+, \xi^-, \varphi) = \frac{1}{\sqrt{2\pi}}\psi(\xi^+, \xi^-)\exp(\mathrm{i}m\varphi).$$

Within these subspaces, the normalization condition on the bound electron states becomes with (19.11),

$$\int_b^\infty d\xi^+ \int_{-b}^b d\xi^- \left[(\xi^+)^2 - (\xi^-)^2\right] \left|\psi(\xi^+, \xi^-)\right|^2 = 8b, \tag{19.14}$$

and the Hamiltonian H_m acting within these subspaces satisfies

$$\frac{m_e}{2\hbar^2}[(\xi^-)^2 - (\xi^+)^2](H_m - E) = D_{+,m}(\xi^+) - D_{-,m}(\xi^-),$$

$$D_{+,m}(\xi^+) = \partial_+ \left((\xi^+)^2 - b^2\right) \partial_+ - \frac{m^2 b^2}{(\xi^+)^2 - b^2} + \frac{m_e}{2\hbar^2} E (\xi^+)^2 + \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2} \xi^+,$$

$$D_{-,m}(\xi^-) = \partial_- \left((\xi^-)^2 - b^2\right) \partial_- - \frac{m^2 b^2}{(\xi^-)^2 - b^2} + \frac{m_e}{2\hbar^2} E (\xi^-)^2.$$

Here the energy E differs from the energy E_e (19.8) of the molecule in the Born-Oppenheimer approximation by the electrostatic energy of the nuclei,

$$E_e = E + \frac{e^2}{4\pi\epsilon_0 b}. \tag{19.15}$$

Since H_m is hermitian with respect to the scalar product appearing in (19.14), the differential operators $D_{+,m}$ and $D_{-,m}$ must be hermitian with respect to the scalar products

$$\langle \psi_+ | \phi_+ \rangle_+ = \int_b^\infty d\xi^+ \, \psi_+^+(\xi^+) \phi_+(\xi^+)$$

and

$$\langle \psi_- | \phi_- \rangle_- = \int_{-b}^b d\xi^+ \, \psi_-^+(\xi^-) \phi_-(\xi^-),$$

respectively. The corresponding Sturm-Liouville type boundary conditions can be read off from the differential operators. We must certainly have

$$\lim_{\xi^+ \to \infty} \psi_+(\xi^+) = 0. \tag{19.16}$$

For azimuthal quantum numbers $m \neq 0$ we must also require

$$\lim_{\xi^+ \to b} \psi_+(\xi^+) = 0, \quad \lim_{\xi^- \to \pm b} \psi_-(\xi^-) = 0. \tag{19.17}$$

Note that $\xi^+ = b$ corresponds to the interval $-b/2 \leq z \leq b/2$ on the z axis, while $\xi^- = -b$ and $\xi^- = b$ correspond to the half-lines $z \leq -b/2$ and $z \geq b/2$ on the z axis, respectively. The boundary conditions (19.17) therefore imply that the wavefunctions

$$\psi_m(\xi^+, \xi^-, \varphi) = \frac{1}{\sqrt{2\pi}} \psi_+(\xi^+) \psi_-(\xi^-) \exp(\mathrm{i} m \varphi)$$

must vanish on the z axis if $m \neq 0$, which apparently makes sense.
We certainly should not expect that the molecular orbitals with $m = 0$ vanish on the z axis, and the differential operators $D_{\pm,0}$ are actually hermitian on their respective domains without extra boundary conditions at $\xi^- = \pm b$ or $\xi^+ = b$ except that the wave functions should remain finite in those points.
The point of this discourse about hermiticity of the operators $D_{\pm,m}$ is that as a consequence, separation of the electronic Schrödinger equation for the hydrogen molecule ion H_2^+ in terms of prolate spheroidal coordinates will not only give us solutions, but a *complete set* of solutions in the form

$$\psi_{m,\lambda}(\xi^+, \xi^-, \varphi) = \frac{1}{\sqrt{2\pi}} \psi_{+,\lambda}(\xi^+)\psi_{-,\lambda}(\xi^-) \exp(\mathrm{i}m\varphi), \tag{19.18}$$

$$D_{-,m}(\xi^-)\psi_{-,\lambda}(\xi^-) = \lambda\psi_{-,\lambda}(\xi^-), \quad -b \leq \xi^- \leq b, \tag{19.19}$$

$$D_{+,m}(\xi^+)\psi_{+,\lambda}(\xi^+) = \lambda\psi_{+,\lambda}(\xi^+). \quad \xi^+ \geq b. \tag{19.20}$$

Energy is a third quantum number which is treated as implicit in the notation for the states.
The equation (19.19) and the equation (19.20) for $e^2 = 0$ are relevant for radiation problems and have been studied extensively, see [1] and references there. The solutions are known as angular spheroidal functions and radial spheroidal functions because of the angular and radial interpretation of the coordinates ξ^- and ξ^+, respectively.
The $\xi^+ \to \infty$ limit of equation (19.20) immediately tells us that we can satisfy the boundary condition (19.16) only for negative energy,

$$\frac{m_e}{2\hbar^2} E = -\kappa^2,$$

and the asymptotic form of the solution should be

$$\psi_{+,\lambda}(\xi^+) = f_{+,\lambda}(\xi^+) \exp(-\kappa\xi^+) \quad \kappa > 0. \tag{19.21}$$

with $\lim_{\xi\to\infty} f_{+,\lambda}(\xi) \exp(-\kappa\xi) = 0$.
We wish to analyze in particular the sector $m = 0$, which should contain the ground state of the H_2^+ ion. Equation (19.20) with $m = 0$ has the form

$$\partial_\xi \left(\xi^2 - b^2\right) \partial_\xi \psi_\lambda(\xi) - \kappa^2\xi^2\psi_\lambda(\xi) + \frac{2}{a_e}\xi\psi_\lambda(\xi) = \lambda\psi_\lambda(\xi), \tag{19.22}$$

where we substituted $\xi^+ \to \xi$, $\psi_+ \to \psi$ because in the following it will be clear from presence or absence of the Coulomb term $\propto 1/a_e$ whether we are considering the radial or the angular spheroidal coordinates and wave functions.
The length parameter

$$a_e = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \frac{\mu}{m_e} a$$

is closely related to the Bohr radius (7.56) of the hydrogen atom.

Since our solution should remain finite at $\xi = b$, we make an *ansatz*

$$\psi_{+,\lambda}(\xi) = \sum_{n\geq 0} c_n \left(\frac{\xi - b}{b}\right)^n \exp[\kappa(b-\xi)]. \tag{19.23}$$

Substitution into (19.22) yields a two-step recursion relation

$$2(n+1)^2 c_{n+1} = \left(\lambda + \kappa^2 b^2 + 2\kappa b - \frac{2b}{a_e} + 4\kappa b n - n(n+1)\right) c_n + 2b\left(\kappa n - \frac{1}{a_e}\right) c_{n-1}. \tag{19.24}$$

On the other hand, $\psi_{-,\lambda}(\xi^-)$ must satisfy the differential equation (19.22) without electrostatic term: $a_e \to \infty$,

$$\partial_\xi \left(\xi^2 - b^2\right) \partial_\xi \psi_\lambda(\xi) - \kappa^2 \xi^2 \psi_\lambda(\xi) = \lambda \psi_\lambda(\xi), \tag{19.25}$$

and on the interval $-b \leq \xi \leq b$. This equation allows for even and odd solutions under $\xi^- \to -\xi^-$, and we expect the ground state solution to be even. Therefore we try an *ansatz*

$$\psi_{-,\lambda}(\xi) = \sum_{n\geq 0} d_n \left(\frac{\xi}{b}\right)^{2n}, \tag{19.26}$$

where we can set e.g.

$$d_0 = 1 \tag{19.27}$$

because the product form $\psi_{+,\lambda}(\xi^+)\psi_{-,\lambda}(\xi^-)/\sqrt{2\pi}$ of the ground state implies a degeneracy between d_0 and the coefficient c_0 in the radial factor (19.23). The constant c_0 is then determined by the normalization condition (19.14). Substitution of (19.26) into (19.25) yields the recursion relation

$$2(n+1)(2n+1)d_{n+1} = \left(4n^2 + 2n - \lambda\right) d_n - \kappa^2 b^2 d_{n-1}. \tag{19.28}$$

The expansions (19.23) and (19.26) are not the standard expansions. For the angular function (19.26) one rather uses an expansion in terms of Legendre polynomials $P_n(\xi/b)$ (or associated Legendre polynomials $P_n^m(\xi/b)$ for $m \neq 0$), which are orthogonal polynomials in $-b \leq \xi \leq b$ and satisfy (19.25) or (19.19) for $\kappa = 0$ and $\lambda = n(n+1)$. For the polynomial factors in the radial function (19.23) one rather uses Laguerre polynomials $L_n(2\kappa(\xi - b))$ or $L_n^m(2\kappa(\xi - b))$, because $L_n^m(2\kappa(\xi - b))\exp[-\kappa(\xi - b)]$ are complete orthogonal functions in $b \leq \xi \leq \infty$. The corresponding two-step recursion relations for the coefficients in these expansions then follow from the differential equations and recursion relations of the orthogonal polynomials. However, for our purposes the simpler expansions (19.23) and (19.26) are sufficient for the illustration of basic solution techniques for the dihydrogen cation.

We cannot go ahead and simply solve the recursion relations (19.24) and (19.28) to some finite order to get approximate wave functions for the electron, because for generic values of λ and $\kappa^2 b^2$ the resulting wave functions will not be regular and square integrable in the domains $-b \le \xi^- \le b$ and $1 \le \xi^+ \le \infty$. Therefore, one first has to determine which pairs of parameters λ and $\kappa^2 b^2$ allow for regular and square integrable solutions.
A classical method for the approximate calculation of the allowed parameter pairs λ and $\kappa^2 b^2$ in a two-step recursion relation like (19.28) uses the ratios

$$f_n = \frac{d_{n+1}}{d_n}$$

with the initial condition from (19.28),

$$f_0 = -\frac{\lambda}{2}.$$

The recursion relation (19.28) can then be written as an upwards recursion $f_{n-1} \to f_n$,

$$f_n = \frac{n}{n+1} - \frac{\lambda}{2(n+1)(2n+1)} - \frac{\kappa^2 b^2}{2(n+1)(2n+1) f_{n-1}}, \tag{19.29}$$

or as a downwards recursion $f_{n+1} \to f_n$,

$$f_n = \frac{\kappa^2 b^2}{2(n+1)(2n+3) - \lambda - 2(n+2)(2n+3) f_{n+1}}. \tag{19.30}$$

The requirement of finite limits $\psi_{-,\lambda}(\pm b)$ of the angular wave function implies that the solution of (19.29,19.30) should satisfy

$$\lim_{n\to\infty} f_n = 0.$$

One way to derive the resulting condition on λ and $\kappa^2 b^2$ in approximate form is to use both relations (19.30) and (19.29) for f_n with the approximation $f_N = 0$ for some $N \gg n$. Iteration of equation (19.30) in $N - n - 1$ steps yields a relation of the form $f_n = f_n^{(-)}(\lambda, \kappa^2 b^2, f_N) \simeq f_n^{(-)}(\lambda, \kappa^2 b^2, 0)$, while on the other hand f_n is also determined in n steps from equation (19.29) and $f_0 = -\lambda/2$: $f_n = f_n^{(+)}(\lambda, \kappa^2 b^2)$. The condition

$$f_n^{(-)}(\lambda, \kappa^2 b^2, 0) = f_n^{(+)}(\lambda, \kappa^2 b^2)$$

then implicitly determines the relation between λ and $\kappa^2 b^2$.
Another way to derive the relation between λ and $\kappa^2 b^2$ writes the recursion relation (19.28) as a matrix relation

$$\underline{F} \cdot \boldsymbol{d} = \lambda \boldsymbol{d}$$

with matrix elements

$$F_{n\geq 0,n'\geq 0} = (4n^2+2n)\delta_{n,n'} - \kappa^2 b^2 \delta_{n,n'+1} - 2(n+1)(2n+1)\delta_{n,n'-1}.$$

The condition

$$\det(\underline{F} - \lambda \underline{1}) = 0 \tag{19.31}$$

is then cut off for an $(N+1)\times(N+1)$ submatrix $F_{0\leq n\leq N, 0\leq n'\leq N}$ to yield a relation between λ and $\kappa^2 b^2$.
Once the relation between λ and $\kappa^2 b^2$ is established, application of the same techniques to (19.24) implies a relation between the remaining parameter $\kappa^2 b^2$ and the parameter b/a_e. Since $\kappa^2 b^2 \propto -E$, this relation determines the quantized energies of the even states (due to the even *ansatz* (19.26)), with $m = 0$. Application of the same techniques with an odd *ansatz* for $\psi_{-,\lambda}(\xi^-)$ or to the equations with general m yields the approximate energy levels and wave functions of the electron in the dihydrogen cation with fixed centers. The matrix and determinant condition for equation (19.24) are

$$\begin{aligned} C_{n\geq 0,n'\geq 0} = &\left(n(n+1) + 2\frac{b}{a_e} - 4n\kappa b - 2\kappa b - \kappa^2 b^2 \right) \delta_{n,n'} \\ &+2b\left(\frac{1}{a_e} - n\kappa\right)\delta_{n,n'+1} + 2(n+1)^2 \delta_{n,n'-1}, \end{aligned}$$

$$\det(\underline{C} - \lambda \underline{1}) = 0 \tag{19.32}$$

Using only 3×3 matrices $\underline{F}$ and $\underline{C}$ in the conditions (19.31) and (19.32) yields a ground state energy

$$E_e = \frac{e^2}{4\pi\epsilon_0 b} - \frac{2\hbar^2}{m_e}\kappa^2 = -14.2\,\mathrm{eV}$$

with eigenvalues $\lambda = -0.490$ and $\kappa b = 1.42$ for a bond length $b = 105$ pm. Using the equivalent of a 4×4 matrix $\underline{F}$ and a 6×6 matrix $\underline{C}$ in the expansions with Legendre and Laguerre polynomials, Aubert *et al.*[8] found $E_e = -16.4$ eV with $\kappa b = 1.485$ for $b = 2a$. Either way, we find that the ground state energy E_e is smaller than the energy $E_1 = -13.6$ eV of a hydrogen atom and a proton at large distance, i.e. sharing the electron stabilizes the dihydrogen cation in spite of the electrostatic repulsion of the protons. The actual dissociation energy $D = E_1 - E_e$ for the dihydrogen cation is about 2.6 eV, i.e. the value of Aubert *et al.* from higher order approximation of the recursion relations is much better, as expected.
The coefficients which follow from the relations (19.24), (19.28), (19.27) and (19.14) for $\lambda = -0.490$ and $\kappa b = 1.42$ are

$$\begin{aligned} &d_0 = 1, \quad d_1 = 0.2451, \quad d_2 = -0.0357, \\ &c_0 = 1.869, \quad c_1 = 0.3760, \quad c_2 = -0.0712. \end{aligned} \tag{19.33}$$

[8] M. Aubert, N. Bessis & G. Bessis, Phys. Rev. A 10, 51 (1974).

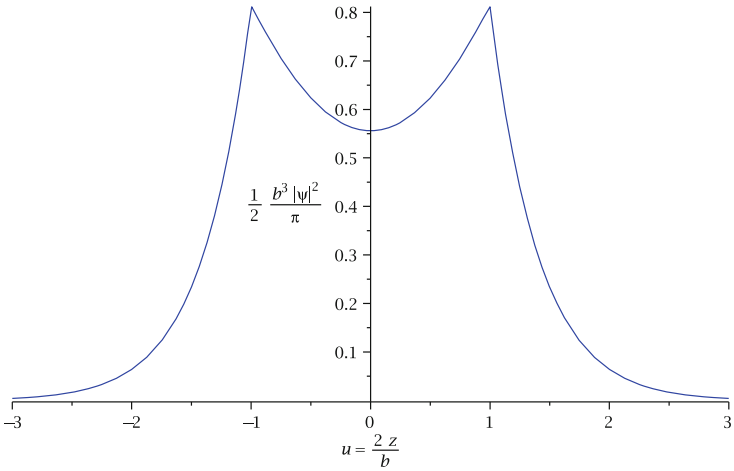


Figure 19.1: The function $b^3|\psi(\xi^+,\xi^-)|^2/2\pi$ for the approximate ground state (19.33) is displayed along the symmetry axis of the dihydrogen cation. The protons are located at $u = \pm 1$. The abscissa $u = 2z/b$ is $u = \xi^-/b$ in the range $-1 < u < 1$, where $\xi^+ = b$. Outside of this range we have $u = -\xi^+/b$ for $u < -1$ ($\xi^- = -b$) and $u = \xi^+/b$ for $u > 1$ ($\xi^- = b$).

The resulting function $b^3|\psi(\xi^+,\xi^-)|^2/2\pi$ along the symmetry axis of the cation is displayed in Figure 19.1. The abscissa u is related to the z coordinate from equation (19.10) through $u = 2z/b$.

This low order approximation has already all the characteristic features of the real ground state as confirmed by higher order approximations. The electronic wave functions fall off with a linear exponential for large values of the radial coodinate ξ^+, and a double peak appears at the locations of the two protons. However, higher order approximations yield lower energies with a corresponding stronger exponential drop $\exp(-\kappa\xi^+)$, $\kappa b > 1.42$. This implies that the values of $b^3|\psi(\xi^+,\xi^-)|^2$ along the symmetry axis are actually underestimated in the aproximation in Figure 19.1, and the cusps become more pronounced in higher order approximations.

Cusps are inevitable in many-particle wave functions for charged particles. Kato had demonstrated that these wave functions have cusps for coalescence of any two charged particles[9]. Specifically, if r_{12} is the separation between two particles with charges $Z_1 e$ and $Z_2 e$, and if the wave function does not vanish

[9] T. Kato, Commun. Pure Appl. Math. 10, 151 (1957). See also R.T. Pack & W.B. Brown, J. Chem. Phys. 45, 556 (1966) and Á. Nagy & C. Amovilli, Phys. Rev. A 82, 042510 (2010).

for $r_{12} \to 0$, the directional average of $\partial\psi/\partial r_{12}$ in the limit $r_{12} \to 0$ satisfies

$$\lim_{r_{12}\to 0} \frac{1}{4\pi} \int_0^\pi d\vartheta \int_0^{2\pi} d\varphi \, \sin\vartheta \frac{\partial\psi}{\partial r_{12}} = \gamma_{12}\psi\Big|_{r_{12}=0}.$$

The constant γ_{12} is

$$\gamma_{12} = Z_1 Z_2 \alpha \frac{\mu_{12} c}{\hbar} = Z_1 Z_2 \frac{\mu_{12}}{m_e} \frac{1}{a_e},$$

where $\mu_{12} = m_1 m_2/(m_1 + m_2)$ is the reduced mass of the charged particles. In particular, coalescence of two electrons or of electrons and protons corresponds to

$$\gamma_{e^-e^-} = \frac{1}{2a_e} \quad \text{and} \quad \gamma_{e^-p^+} = -\frac{1}{a}.$$

19.3 Bloch and Wannier operators

The use of second quantized Hamiltonians is ubiquitous in condensed matter physics, and in the following sections we will introduce very common and useful examples for this, viz. the Hubbard Hamiltonian for electron-electron interactions, phonons, and a basic Hamiltonian for electron-phonon coupling. We will motivate the model Hamiltonians from basic Schrödinger field theory or the classical Hamiltonian for lattice vibrations, respectively, and refer the reader to more specialized monographs for alternative derivations of these Hamiltonians.

However, before we embark on this journey, we should generalize the results from Sections 10.1, 10.2 and 10.3 to three dimensions and combine them with what we had learned in Chapter 17 about quantization and Schrödinger field operators.

The basic Schrödinger picture Hamiltonian for an electron gas has the form

$$\begin{aligned} H &= \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \sum_{\sigma,\sigma'} \psi_\sigma^+(\boldsymbol{x})\psi_{\sigma'}^+(\boldsymbol{x}') \frac{e^2}{8\pi\epsilon_0 \left|\boldsymbol{x}-\boldsymbol{x}'\right|} \psi_{\sigma'}(\boldsymbol{x}')\psi_\sigma(\boldsymbol{x}) \\ &\quad + \int d^3\boldsymbol{x} \sum_\sigma \frac{\hbar^2}{2m} \boldsymbol{\nabla}\psi_\sigma^+(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\psi_\sigma(\boldsymbol{x}) \\ &= \int d^3\boldsymbol{k} \int d^3\boldsymbol{k}' \int d^3\boldsymbol{q} \sum_{\sigma,\sigma'} a_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) a_{\sigma'}^+(\boldsymbol{k}'-\boldsymbol{q}) \frac{e^2}{16\pi^3\epsilon_0 \boldsymbol{q}^2} a_{\sigma'}(\boldsymbol{k}') a_\sigma(\boldsymbol{k}) \\ &\quad + \int d^3\boldsymbol{k} \sum_\sigma \frac{\hbar^2\boldsymbol{k}^2}{2m} a_\sigma^+(\boldsymbol{k}) a_\sigma(\boldsymbol{k}). \end{aligned} \tag{19.34}$$

Suppose that this electron gas exists in a lattice with basis vectors $\boldsymbol{a}_i$ and dual basis vectors $\boldsymbol{a}^i$ (4.12). The lattice points are $\boldsymbol{\ell} = n^i \boldsymbol{a}_i$ with a triplet of integers n^i. However, we can also use the basis $\boldsymbol{a}_i$ as a basis in $\mathbb{R}^3$,

$$\boldsymbol{x} = x^i \boldsymbol{e}_i = \nu^i \boldsymbol{a}_i, \quad \boldsymbol{\nabla} = \boldsymbol{e}^i \frac{\partial}{\partial x^i} = \boldsymbol{a}^i \frac{\partial}{\partial \nu^i}.$$

Note that the coordinates x^i and the lattice basis vectors $\boldsymbol{a}_i$ have the dimensions of length, while the dual basis vectors have dimension length^{-1}. The coordinates ν^i are dimensionless.
A Brillouin zone $\mathcal{B}$ is a unit cell in the dual lattice stretched by a factor 2π and then shifted such that the center of the Brillouin zone is a dual lattice point,

$$\boldsymbol{k} = \kappa_i \boldsymbol{a}^i, \quad -\pi < \kappa_i \leq \pi, \tag{19.35}$$

see also (10.6), where this notion was introduced for one-dimensional lattices. The $\boldsymbol{k}$ vectors in a Brillouin zone have the following useful properties, which are easily derived from Fourier transformation on a one-dimensional lattice[10]
$\kappa_i \equiv \kappa_i + 2\pi$,

$$\int_{\mathcal{B}} d^3\boldsymbol{k}\, \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{\ell}-\boldsymbol{\ell}')] = (2\pi)^3 \tilde{V}\delta_{\boldsymbol{\ell},\boldsymbol{\ell}'}, \quad d^3\boldsymbol{k} = \tilde{V} d\kappa_1 d\kappa_2 d\kappa_3, \tag{19.36}$$

$$\sum_{\boldsymbol{\ell}} \exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{\ell}] = (2\pi)^3 \tilde{V}\delta(\boldsymbol{k}-\boldsymbol{k}'). \tag{19.37}$$

Recall that the volume of a unit cell $\tilde{V}$ in the dual lattice is related to the volume of a unit cell in the direct lattice through $\tilde{V} = 1/V$, (4.13).
If a unit cell in the lattice contains N ions, electrons in the lattice will also experience a lattice potential

$$H_V(\boldsymbol{x}) = -\sum_{\boldsymbol{\ell},A} \frac{n_A e^2}{4\pi\epsilon_0\,|\boldsymbol{x}-\boldsymbol{r}_{\boldsymbol{\ell},A}|}, \tag{19.38}$$

where

$$\boldsymbol{r}_{\boldsymbol{\ell},A} = \boldsymbol{\ell} + \boldsymbol{r}_A \quad 1 \leq A \leq N,$$

enumerates the locations of the ions in the unit cell $\boldsymbol{\ell} = n^i\boldsymbol{a}_i$, and $n_A e$ is the effective charge of the A-th ion. On the level of the quantized Schrödinger field theory, the potential (19.38) adds the operator

$$H_V = -\sum_{\boldsymbol{\ell},A} \int d^3\boldsymbol{x} \sum_\sigma \psi^+_\sigma(\boldsymbol{x}) \frac{n_A e^2}{4\pi\epsilon_0\,|\boldsymbol{x}-\boldsymbol{r}_{\boldsymbol{\ell},A}|} \psi_\sigma(\boldsymbol{x}), \tag{19.39}$$

to the Hamiltonian (19.34). We will focus on this potential term in the remainder of this section and neglect the electron-electron interaction term in (19.34). The corresponding first quantized Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + H_V(\mathbf{x}),$$

[10] We have seen the corresponding one-dimensional equations in (10.1-10.4). However, when comparing equations (19.36) and (19.37) with (10.1-10.4) please keep in mind that the continuous variables κ_i play the role of x there, while the discrete lattice sites $\boldsymbol{\ell} = n^i\boldsymbol{a}_i$ compare to the discrete momenta $2\pi n/a$ in equations (10.1-10.4), see also (10.8).

is invariant under lattice translations,

$$\exp\left(\frac{\mathrm{i}}{\hbar}\boldsymbol{\ell}\cdot\mathbf{p}\right) H \exp\left(-\frac{\mathrm{i}}{\hbar}\boldsymbol{\ell}\cdot\mathbf{p}\right) = \frac{\mathbf{p}^2}{2m} + H_V(\mathbf{x}+\boldsymbol{\ell}) = H,$$

and therefore admits a complete set of Bloch type eigenstates, see (10.10) for the one-dimensional case. We can decompose the Schrödinger picture field operators $\psi_\sigma(\boldsymbol{x})$ in terms of a complete set of Bloch type eigenstates

$$\psi_\sigma(\boldsymbol{x}) = \sum_n \sqrt{\frac{V}{(2\pi)^3}} \int_{\mathcal{B}} d^3\boldsymbol{k}\, a_{n,\sigma}(\boldsymbol{k}) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) u_n(\boldsymbol{k},\boldsymbol{x}), \tag{19.40}$$

$$a_{n,\sigma}(\boldsymbol{k}) = \sqrt{\frac{V}{(2\pi)^3}} \int d^3\boldsymbol{x}\, \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) u_n^+(\boldsymbol{k},\boldsymbol{x}) \psi_\sigma(\boldsymbol{x}), \tag{19.41}$$

with periodic Bloch factors

$$u_n(\boldsymbol{k},\boldsymbol{x}+\boldsymbol{\ell}) = u_n(\boldsymbol{k},\boldsymbol{x}).$$

We denote integration over the unit cell of the lattice with $\int_V d^3\boldsymbol{x}$. Normalization of the Bloch energy eigenfunctions then yields

$$\begin{aligned}\delta_{mn}\delta(\boldsymbol{k}-\boldsymbol{k}') &= \frac{V}{(2\pi)^3}\int d^3\boldsymbol{x}\, \exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}] u_m^+(\boldsymbol{k}',\boldsymbol{x}) u_n(\boldsymbol{k},\boldsymbol{x}) \\ &= \frac{V}{(2\pi)^3}\sum_{\boldsymbol{\ell}} \exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{\ell}] \\ &\quad \times \int_V d^3\boldsymbol{x}\, \exp[\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}] u_m^+(\boldsymbol{k}',\boldsymbol{x}) u_n(\boldsymbol{k},\boldsymbol{x}),\end{aligned} \tag{19.42}$$

and with (19.37) we find

$$\int_V d^3\boldsymbol{x}\, u_m^+(\boldsymbol{k},\boldsymbol{x}) u_n(\boldsymbol{k},\boldsymbol{x}) = \delta_{mn}.$$

Equation (19.42) also implies with the canonical anticommutation relations for the Schrödinger field operators $\psi_\sigma(\boldsymbol{x})$ and $\psi_\sigma^+(\boldsymbol{x})$ that the the operators $a_{n,\sigma}(\boldsymbol{k})$ satisfy the relations

$$\{a_{n,\sigma}(\boldsymbol{k}), a_{n',\sigma'}(\boldsymbol{k}')\} = 0 \quad \{a_{n,\sigma}(\boldsymbol{k}), a^+_{n',\sigma'}(\boldsymbol{k}')\} = \delta_{n,n'}\delta_{\sigma,\sigma'}\delta(\boldsymbol{k}-\boldsymbol{k}').$$

The second quantized state

$$|n,\sigma,\boldsymbol{k}\rangle = a^+_{n,\sigma}(\boldsymbol{k})|0\rangle$$

is therefore a state with an electron in the first quantized orbital Bloch state

$$\phi_n(\boldsymbol{k},\boldsymbol{x}) = \sqrt{\frac{V}{(2\pi)^3}} \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) u_n(\boldsymbol{k},\boldsymbol{x}) \tag{19.43}$$

and spin projection σ. Equation (19.41) and the conjugate equation for $a^+_{n,\sigma}(\boldsymbol{k})$ are a special case of our general observations (17.44) and (17.43) how annihilation and creation operators for particles in specific states relate to the generic operators $\psi_\sigma(\boldsymbol{x})$ and $\psi^+_\sigma(\boldsymbol{x})$.
Since the operators $a_{n,\sigma}(\boldsymbol{k})$ are restricted to the Brillouin zone, or equivalently are periodic in the rescaled dual lattice with the Brillouin zone as unit cell,

$$a_{n,\sigma}(\boldsymbol{k}) = a_{n,\sigma}(\boldsymbol{k} + 2\pi\tilde{\boldsymbol{\ell}}), \quad \tilde{\boldsymbol{\ell}} = n_i \boldsymbol{a}^i,$$

we can expand them using equations (19.36,19.37),

$$a^+_{n,\sigma}(\boldsymbol{k}) = \sqrt{\frac{V}{(2\pi)^3}} \sum_{\boldsymbol{\ell}} \psi^+_{n,\sigma}(\boldsymbol{\ell}) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}), \tag{19.44}$$

$$\psi^+_{n,\sigma}(\boldsymbol{\ell}) = \sqrt{\frac{V}{(2\pi)^3}} \int_{\mathcal{B}} d^3\boldsymbol{k}\, a^+_{n,\sigma}(\boldsymbol{k}) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}). \tag{19.45}$$

The operators $\psi_{n,\sigma}(\boldsymbol{\ell})$ in the direct lattice satisfy

$$\{\psi_{n,\sigma}(\boldsymbol{\ell}), \psi_{n',\sigma'}(\boldsymbol{\ell}')\} = 0 \quad \{\psi_{n,\sigma}(\boldsymbol{\ell}), \psi^+_{n',\sigma'}(\boldsymbol{\ell}')\} = \delta_{n,n'}\delta_{\sigma,\sigma'}\delta(\boldsymbol{\ell} - \boldsymbol{\ell}').$$

Substitution of (19.41) into (19.45) yields

$$\psi^+_{n,\sigma}(\boldsymbol{\ell}) = \int d^3\boldsymbol{x}\, w_n(\boldsymbol{\ell}, \boldsymbol{x}) \psi^+_\sigma(\boldsymbol{x})$$

with the Wannier states

$$w_n(\boldsymbol{\ell}, \boldsymbol{x}) = \frac{V}{(2\pi)^3} \int_{\mathcal{B}} d^3\boldsymbol{k}\, u_n(\boldsymbol{k}, \boldsymbol{x}) \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x} - \boldsymbol{\ell})] = w_n(\boldsymbol{x} - \boldsymbol{\ell}). \tag{19.46}$$

These states satisfy the usual completeness relations as a consequence of the completeness relations of the Bloch states $\phi_n(\boldsymbol{k}, \boldsymbol{x})$,

$$\int d^3\boldsymbol{x}\, w^+_n(\boldsymbol{\ell}, \boldsymbol{x}) w_{n'}(\boldsymbol{\ell}', \boldsymbol{x}) = \delta_{n,n'}\delta_{\boldsymbol{\ell},\boldsymbol{\ell}'},$$

$$\sum_{n,\boldsymbol{\ell}} w_n(\boldsymbol{\ell}, \boldsymbol{x}) w^+_n(\boldsymbol{\ell}, \boldsymbol{x}') = \delta(\boldsymbol{x} - \boldsymbol{x}').$$

The operator $\psi^+_{n,\sigma}(\boldsymbol{\ell})$ therefore generates an electron with spin projection σ in the Wannier state $w_n(\boldsymbol{\ell}, \boldsymbol{x})$.
We denote the operators $a_{n,\sigma}(\boldsymbol{k})$ and $a^+_{n,\sigma}(\boldsymbol{k})$ as Bloch operators, and the operators $\psi_{n,\sigma}(\boldsymbol{\ell})$ and $\psi^+_{n,\sigma}(\boldsymbol{\ell})$ as Wannier operators.

19.4 The Hubbard model

The Hubbard model treats electron-electron interactions in a tight binding approximation. Therefore we wish to use the creation operators $\psi^+_{n,\sigma}(\boldsymbol{\ell})$ for electrons in Wannier states.
The kinetic electron operator transforms into Wannier type operators according to

$$\begin{aligned} H_0 &= \int d^3\boldsymbol{x} \sum_\sigma \frac{\hbar^2}{2m} \boldsymbol{\nabla}\psi^+_\sigma(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\psi_\sigma(\boldsymbol{x}) \\ &= \int d^3\boldsymbol{x} \sum_{\sigma,n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} \psi^+_{n,\sigma}(\boldsymbol{\ell}) \frac{\hbar^2}{2m} \boldsymbol{\nabla} w^+_n(\boldsymbol{\ell},\boldsymbol{x}) \cdot \boldsymbol{\nabla} w_{n'}(\boldsymbol{\ell}',\boldsymbol{x}) \psi_{n',\sigma}(\boldsymbol{\ell}'). \end{aligned} \tag{19.47}$$

This has the form of a hopping Hamiltonian for jumps $n', \boldsymbol{\ell}' \to n, \boldsymbol{\ell}$,

$$H_0 = \sum_{\sigma,n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} t_{n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} \psi^+_{n,\sigma}(\boldsymbol{\ell}) \psi_{n',\sigma}(\boldsymbol{\ell}') \tag{19.48}$$

with a hopping parameter

$$t_{n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} = \int d^3\boldsymbol{x} \, \frac{\hbar^2}{2m} \boldsymbol{\nabla} w^+_n(\boldsymbol{\ell},\boldsymbol{x}) \cdot \boldsymbol{\nabla} w_{n'}(\boldsymbol{\ell}',\boldsymbol{x}).$$

On the other hand, the electron-electron interaction Hamiltonian becomes

$$H_{ee} = \frac{1}{2} \sum_{\sigma,\sigma',m,\boldsymbol{l},m',\boldsymbol{l}',n,\boldsymbol{\ell},n',\boldsymbol{\ell}'} U_{m,\boldsymbol{l},m',\boldsymbol{l}',n',\boldsymbol{\ell}',n,\boldsymbol{\ell}} \psi^+_{m,\sigma}(\boldsymbol{l}) \psi^+_{m',\sigma'}(\boldsymbol{l}') \psi_{n',\sigma'}(\boldsymbol{\ell}') \psi_{n,\sigma}(\boldsymbol{\ell})$$

with the Coulomb matrix element

$$\begin{aligned} U_{m,\boldsymbol{l},m',\boldsymbol{l}',n',\boldsymbol{\ell}',n,\boldsymbol{\ell}} = \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}' \, w^+_m(\boldsymbol{l},\boldsymbol{x}) w^+_{m'}(\boldsymbol{l}',\boldsymbol{x}') \\ \times \frac{e^2}{4\pi\epsilon_0 \, |\boldsymbol{x}-\boldsymbol{x}'|} w_{n'}(\boldsymbol{\ell}',\boldsymbol{x}') w_n(\boldsymbol{\ell},\boldsymbol{x}). \end{aligned}$$

H_{ee} would certainly be dominated by terms on the same lattice site, and if we restrict the discussion to a single band index, the electron-electron interaction Hamiltonian $H = H_0 + H_{ee}$ assumes the simple form

$$H = \sum_{\boldsymbol{\ell},\boldsymbol{\ell}',\sigma} t_{\boldsymbol{\ell},\boldsymbol{\ell}'} \psi^+_\sigma(\boldsymbol{\ell}) \psi_\sigma(\boldsymbol{\ell}') + U \sum_{\boldsymbol{\ell}} n_{\uparrow,\boldsymbol{\ell}} n_{\downarrow,\boldsymbol{\ell}}, \tag{19.49}$$

with the spin polarized occupation number operators for lattice site $\boldsymbol{\ell}$,

$$n_{\sigma,\boldsymbol{\ell}} = \psi^+_\sigma(\boldsymbol{\ell}) \psi_\sigma(\boldsymbol{\ell}).$$

The Hamiltonian (19.49) is known as the *Hubbard Hamiltonian*[11]. This Hamiltonian was invented for the analysis of ferromagnetic behavior in transition

[11] J. Hubbard, Proc. Roy. Soc. London A 276, 238 (1963), see also M.C. Gutzwiller, Phys. Rev. Lett. 10, 159 (1963).

metals, and soon became a very widely used model Hamiltonian in condensed matter theory not only for magnetic ordering, but also for the general investigation of electron correlations, conductivity properties and disorder effects in many different classes of materials[12]. However, the Hubbard model also provides basic insight into the relevance of delocalized Bloch states versus localized Wannier states, as we will now discuss.

We assume that the hopping term is invariant under translation and symmetric between sites, i.e.

$$t_{\boldsymbol{\ell},\boldsymbol{\ell}'} = t_{\boldsymbol{\ell}-\boldsymbol{\ell}'} = t_{\Delta\boldsymbol{\ell}} = t_{-\Delta\boldsymbol{\ell}}.$$

If hopping is suppressed,

$$t_{\boldsymbol{\ell},\boldsymbol{\ell}'} = t\delta_{\boldsymbol{\ell},\boldsymbol{\ell}'},$$

the Hamiltonian involves only the number operators $n_{\sigma,\boldsymbol{\ell}}$,

$$H = t\sum_{\sigma,\boldsymbol{\ell}} n_{\sigma,\boldsymbol{\ell}} + U\sum_{\boldsymbol{\ell}} n_{\uparrow,\boldsymbol{\ell}} n_{\downarrow,\boldsymbol{\ell}}, \tag{19.50}$$

and the eigenstates and energy levels are given by $N = N_1 + 2N_2$ particle states

$$|\sigma_1, \boldsymbol{\ell}_1; \ldots \sigma_N, \boldsymbol{\ell}_N\rangle = \psi^+_{\sigma_1}(\boldsymbol{\ell}_1)\ldots\psi^+_{\sigma_N}(\boldsymbol{\ell}_N)|0\rangle$$

with energy

$$E(N_1, N_2) = t(N_1 + 2N_2) + UN_2.$$

Here N_1 and N_2 are the numbers of single and double occupied lattice sites, respectively. This is also denoted as the atomic limit, since the electrons are fixed at the atoms and the total energy is a sum of atomic terms.

On the other hand, if we can neglect the electron-electron interaction term, $U = 0$, we end up with a quadratic Hamiltonian

$$H = \sum_{\boldsymbol{\ell},\Delta\boldsymbol{\ell},\sigma} t_{\Delta\boldsymbol{\ell}}\psi^+_\sigma(\boldsymbol{\ell} + \Delta\boldsymbol{\ell})\psi_\sigma(\boldsymbol{\ell}). \tag{19.51}$$

We can map the electron operators on lattice sites to electron operators (19.44) in the Brillouin zone,

$$a_\sigma(\boldsymbol{k}) = \frac{\sqrt{V}}{\sqrt{2\pi}^3}\sum_{\boldsymbol{\ell}} \psi_\sigma(\boldsymbol{\ell})\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}), \tag{19.52}$$

This diagonalizes the Hamiltonian (19.51),

$$H = \int_{\mathcal{B}} d^3\boldsymbol{k}\, E(\boldsymbol{k})\sum_\sigma a^+_\sigma(\boldsymbol{k})a_\sigma(\boldsymbol{k}), \tag{19.53}$$

[12] See e.g. J.E. Hirsch, Phys. Rev. B 31, 4403 (1985); I. Affleck & J.B. Marston, Phys. Rev. B 37, 3774 (1988); Y.M. Vilk & A.-M.S. Tremblay, J. Physique I 7, 1309 (1997). More comprehensive textbook discussions can be found in references [4, 10].

$$E(\boldsymbol{k}) = \sum_{\Delta\boldsymbol{\ell}} t_{\Delta\boldsymbol{\ell}} \exp(-\mathrm{i}\boldsymbol{k}\cdot\Delta\boldsymbol{\ell}) = \sum_{\Delta\boldsymbol{\ell}} t_{\Delta\boldsymbol{\ell}} \cos(\boldsymbol{k}\cdot\Delta\boldsymbol{\ell}). \tag{19.54}$$

The single particle eigenstate of the Hamiltonian (19.53) with energy $E(\boldsymbol{k})$,

$$a^+_\sigma(\boldsymbol{k})|0\rangle = \frac{\sqrt{V}}{\sqrt{2\pi}^3} \sum_{\boldsymbol{\ell}} \psi^+_\sigma(\boldsymbol{\ell}) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell})|0\rangle,$$

is a Bloch state, while the single particle eigenstate $\psi^+_\sigma(\boldsymbol{\ell})|0\rangle$ of the Hamiltonian (19.50) is a Wannier state. The magnitude of the hopping terms $t_{\Delta\boldsymbol{\ell}\neq\mathbf{0}}$ relative to U will therefore determine the importance of itinerant (or delocalized) Bloch electron states versus localized Wannier electron states in the lattice.

19.5 Vibrations in molecules and lattices

Another basic excitation of lattices concerns oscillations of lattice ions or atoms around their equilibrium configurations. This kind of excitation is particularly amenable to description in classical mechanical terms, but at the quantum level lattice vibrations are very similar to quantum excitations of the vacuum like electrons or photons. In particular, elementary lattice vibrations can be spontaneously created and absorbed like photons, and therefore require a quantum field theory which is similar to the field theory for photons.
We will discuss the classical theory of small oscillations of N-particle systems in the present section as a preparation for the discussion of quantized lattice vibrations in Section 19.6. We suspend summation convention in this section, because we often encounter expressions with three identical indices in a multiplicative term, and also terms like $m_i \ddot{x}_i{}^j$ without summation over the repeated index.

Normal coordinates and normal oscillations

We consider an N particle system with potential $V(\boldsymbol{r}_1, \ldots \boldsymbol{r}_N)$. The equilibrium condition

$$\nabla_i V(\boldsymbol{r}_1, \ldots \boldsymbol{r}_N)\Big|_{\boldsymbol{r}_j = \boldsymbol{r}_j^{(0)}} = \mathbf{0} \tag{19.55}$$

implies for the second order expansion around an equilibrium configuration $\boldsymbol{r}_1^{(0)}, \ldots \boldsymbol{r}_N^{(0)}$,

$$V(\boldsymbol{r}_1, \ldots \boldsymbol{r}_N) = V(\boldsymbol{r}_1^{(0)}, \ldots \boldsymbol{r}_N^{(0)}) + \frac{1}{2} \sum_{ijkl} V_{ik,jl} x_i{}^k x_j{}^l,$$

where $\boldsymbol{x}_i = \boldsymbol{r}_i - \boldsymbol{r}_i^{(0)}$ parametrize the deviations from equilibrium and the coefficients $V_{ik,jl}$ are

$$V_{ik,jl} = \frac{\partial^2}{\partial y_i{}^k \partial y_j{}^l} V(\boldsymbol{r}_1^{(0)} + \boldsymbol{y}_1, \ldots \boldsymbol{r}_N^{(0)} + \boldsymbol{y}_N)\Big|_{\boldsymbol{y}_m = \mathbf{0}}.$$

The second order Lagrange function for small oscillations of the system,

$$L = \frac{1}{2}\sum_{ik} m_i \dot{x}_i{}^k \dot{x}_i{}^k - \frac{1}{2}\sum_{ijkl} V_{ik,jl} x_i{}^k x_j{}^l, \tag{19.56}$$

yields $3N$ coupled equations of motion

$$m_i \ddot{x}_i{}^k = -\sum_{jl} V_{ik,jl} x_j{}^l. \tag{19.57}$$

Fourier transformation

$$x_i{}^k(t) = \int d\omega\, a_i{}^k(\omega) \exp(-\mathrm{i}\omega t), \quad [a_i{}^k(\omega)]^+ = a_i{}^k(-\omega), \tag{19.58}$$

yields the conditions

$$\sum_{jl} (V_{ik,jl} - m_i \omega^2 \delta_{ij}\delta_{kl}) a_j{}^l(\omega) = 0. \tag{19.59}$$

Writing this in the form

$$\sum_{jl} \left(\frac{V_{ik,jl}}{\sqrt{m_i m_j}} - \omega^2 \delta_{ij}\delta_{kl} \right) \sqrt{m_j}\, a_j{}^l(\omega) = 0$$

tells us that the $3N$-dimensional vector

$$\boldsymbol{Q}(\omega) = \{\sqrt{m_1} a_1{}^1(\omega), \ldots \sqrt{m_N} a_N{}^3(\omega)\} = \boldsymbol{Q}^+(-\omega) \tag{19.60}$$

must have the form

$$\boldsymbol{Q}(\omega) = \sum_{I=1}^{3N} \left[\boldsymbol{Q}_I \delta(\omega - \omega_I) + \boldsymbol{Q}_{-I} \delta(\omega + \omega_I) \right], \tag{19.61}$$

where $\boldsymbol{Q}_I = \{\sqrt{m_1} a_{I,1}{}^1, \ldots \sqrt{m_N} a_{I,N}{}^3\} = \boldsymbol{Q}^+_{-I}$ is an eigenvector of the symmetric $3N \times 3N$ matrix

$$\Omega^2_{ik,jl} = \frac{V_{ik,jl}}{\sqrt{m_i m_j}} \tag{19.62}$$

with eigenvalue ω_I^2. We assume that $\boldsymbol{r}_1^{(0)}, \ldots \boldsymbol{r}_N^{(0)}$ is a stable equilibrium configuration such that all eigenvalues of $\Omega^2_{ik,jl}$ satisfy $\omega_I^2 \geq 0$, and we define $\omega_I = \sqrt{\omega_I^2} \geq 0$ as the positive semi-definite roots.
Since $\underline{\Omega^2}$ is a symmetric real $3N \times 3N$ matrix, we can find $3N$ orthogonal normalized real vectors

$$\hat{\boldsymbol{Q}}_I = \{\sqrt{m_1} \hat{a}_{I,1}{}^1, \ldots \sqrt{m_N} \hat{a}_{I,N}{}^3\}$$

which solve the eigenvalue problem

$$\underline{\Omega^2} \cdot \hat{\boldsymbol{Q}}_I = \omega_I^2 \hat{\boldsymbol{Q}}_I. \tag{19.63}$$

The general solution $\boldsymbol{Q}_I$ (19.60) of the eigenvalue problem with eigenvalue ω_I^2 will then have the form

$$\boldsymbol{Q}_I = q_I \hat{\boldsymbol{Q}}_I$$

with arbitrary complex factors $q_I = |q_I| \exp(\mathrm{i}\varphi_I)$. The mode expansion (19.58) will therefore take the form

$$\begin{aligned} x_i{}^k(t) &= \sum_{I=1}^{3N} \hat{a}_{I,i}{}^k \left[q_I \exp(-\mathrm{i}\omega_I t) + q_I^+ \exp(\mathrm{i}\omega_I t) \right] \\ &= 2 \sum_{I=1}^{3N} \hat{a}_{I,i}{}^k \, |q_I| \left[\cos(\varphi_I) \cos(\omega_I t) + \sin(\varphi_I) \sin(\omega_I t) \right]. \end{aligned} \tag{19.64}$$

Equation (19.63) and $V_{ik,jl} = V_{jl,ik} = V_{ik,jl}^+$ imply the orthogonality relations

$$0 = \sum_{ijkl} (\hat{a}_{I,i}{}^k V_{ik,jl} \hat{a}_{J,j}{}^l - \hat{a}_{I,i}{}^k V_{ik,jl} \hat{a}_{J,j}{}^l) = \sum_{ik} m_i \hat{a}_{\pm I,1}{}^k \hat{a}_{J,j}{}^k (\omega_I^2 - \omega_J^2).$$

This yields

$$\sum_{ik} m_i \hat{a}_{I,i}{}^k \hat{a}_{J,i}{}^k = \delta_{IJ}, \tag{19.65}$$

where we assume that eigenvectors $\hat{\boldsymbol{Q}}_I$ within degeneracy subspaces have been orthonormalized.

Note that the normalization changes the dimensions and the physical meaning of the coefficients. The amplitudes $a_{I,i}{}^k$ in equation (19.64) have the dimensions of a length, and the related eigenvectors $\boldsymbol{Q}_I$ and factors q_I have the dimension of mass$^{1/2}$ × length. The normalized eigenvectors $\hat{\boldsymbol{Q}}_I$ are dimensionless, and therefore the related coefficients $\hat{a}_{I,i}{}^k$ have dimension mass$^{-1/2}$. We will denote the related $3N$ dimensional vector $\hat{\boldsymbol{a}}_I = \{\hat{a}_{I,1}{}^1, \ldots, \hat{a}_{I,N}{}^3\}$ as an *amplitude vector*.

The small oscillations of the system are then determined by the eigenmodes $\hat{\boldsymbol{a}}_I$ (or equivalently $\hat{\boldsymbol{Q}}_I$), and how strongly these eigenmodes of oscillation are excited,

$$x_i{}^k(t) = \sum_{I=1}^{3N} \hat{a}_{I,i}{}^k \left[q_I \exp(-\mathrm{i}\omega_I t) + q_I^+ \exp(\mathrm{i}\omega_I t) \right], \tag{19.66}$$

$$\dot{x}_i{}^k(t) = -\mathrm{i} \sum_{I=1}^{3N} \omega_I \hat{a}_{I,i}{}^k \left[q_I \exp(-\mathrm{i}\omega_I t) - q_I^+ \exp(\mathrm{i}\omega_I t) \right], \tag{19.67}$$

$$q_I = \frac{1}{2} \exp(\mathrm{i}\omega_I t) \sum_{ik} m_i \hat{a}_{I,i}{}^k \left(x_i{}^k(t) + \frac{\mathrm{i}}{\omega_I} \dot{x}_i{}^k(t) \right). \tag{19.68}$$

The $3N$ complex amplitudes q_I are denoted as *normal coordinates* of the oscillating N particle system, and the related eigenmodes of oscillation are also denoted as *normal modes*. Note from equations (19.66) or (19.68) that we can think of the coefficients $\hat{a}_{I,i}{}^k$ also as the components of a $3N \times 3N$ transformation matrix between the $3N$ Cartesian coordinates $x_i{}^k(t)$ and the $3N$ normal coordinates q_I of the oscillating system. These $3N \times 3N$ matrices satisfy the mass weighted orthogonality properties (19.65) and

$$\sum_I \hat{a}_{I,i}{}^k \hat{a}_{I,j}{}^l = \frac{1}{m_i}\delta_{ij}\delta^{kl}, \tag{19.69}$$

which follows from re-substitution of q_I (19.68) into $x_i{}^k(t)$ (19.66).

Appearance of the particular eigenvalue $\omega_I^2 = 0$ implies that the system is symmetric under rotations or translations. The corresponding amplitude vectors $\hat{\boldsymbol{a}}_I = \{\hat{a}_{I,i}{}^k\}$ denote the tangential directions to rotations or translations of the system.

We have learned that small oscillations of a system are always superpositions of the normal oscillation modes or eigenoscillations of the system. *A priori* this does not seem to be particularly helpful to determine the actual small oscillations of a system, because finding the eigenmodes is equivalent to the diagonalization of the $3N \times 3N$ matrix $\Omega^2_{ik,jl}$, which is anyhow the main task in the solution of the equations of motion (19.57) using the Fourier *ansatz* (19.64).

However, if the equilibrium configuration of the system has symmetries, then we can often guess the form of some of the eigenmodes wich leaves us with a smaller diagonalization problem for the determination of the remaining eigenmodes.

Eigenmodes of three masses

A simple example for the identification of normal modes of a coupled particle system is given by three identical masses in a regular triangle, see Figure 19.2. We will determine the eigenmodes in the plane of the triangle. The potential of the coupled system in the harmonic approximation is

$$\begin{aligned} V &= \frac{K}{2}\Big((|\boldsymbol{r}_1 - \boldsymbol{r}_2| - d)^2 + (|\boldsymbol{r}_1 - \boldsymbol{r}_3| - d)^2 + (|\boldsymbol{r}_2 - \boldsymbol{r}_3| - d)^2\Big) \\ &\simeq \frac{K}{2}\Big((x_1{}^1 - x_2{}^1)^2 + \frac{1}{4}(x_1{}^1 - x_3{}^1)^2 + \frac{1}{4}(x_2{}^1 - x_3{}^1)^2 + \frac{3}{4}(x_1{}^2 - x_3{}^2)^2 \\ &\quad + \frac{3}{4}(x_2{}^2 - x_3{}^2)^2 + \frac{\sqrt{3}}{2}(x_1{}^1 x_1{}^2 - x_1{}^1 x_3{}^2 - x_2{}^1 x_2{}^2 + x_2{}^1 x_3{}^2 \\ &\quad - x_3{}^1 x_1{}^2 + x_3{}^1 x_2{}^2)\Big). \end{aligned}$$

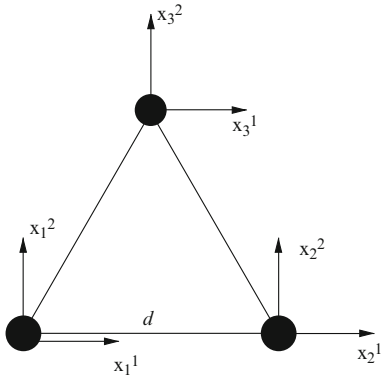


Figure 19.2: Three elastically bound masses with equilibrium distance d.

The matrix $V_{ik,jl}$ is

$$\underline{V} = m\underline{\Omega^2} = K \begin{pmatrix} \frac{5}{4} & \frac{\sqrt{3}}{4} & -1 & 0 & -\frac{1}{4} & -\frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{3}{4} & 0 & 0 & -\frac{\sqrt{3}}{4} & -\frac{3}{4} \\ -1 & 0 & \frac{5}{4} & -\frac{\sqrt{3}}{4} & -\frac{1}{4} & \frac{\sqrt{3}}{4} \\ 0 & 0 & -\frac{\sqrt{3}}{4} & \frac{3}{4} & \frac{\sqrt{3}}{4} & -\frac{3}{4} \\ -\frac{1}{4} & -\frac{\sqrt{3}}{4} & -\frac{1}{4} & \frac{\sqrt{3}}{4} & \frac{1}{2} & 0 \\ -\frac{\sqrt{3}}{4} & -\frac{3}{4} & \frac{\sqrt{3}}{4} & -\frac{3}{4} & 0 & \frac{3}{2} \end{pmatrix},$$

and we must have

$$\mathrm{Det}(\underline{V} - m\omega^2 \underline{\mathbf{1}}) = 0.$$

Absence of external forces on the coupled system implies that there must be two translational and one rotational eigenmode, see Figures 19.2 and 19.3,

$$\hat{\boldsymbol{Q}}_1 = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \quad \hat{\boldsymbol{Q}}_2 = \frac{1}{\sqrt{3}} \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix}, \quad \hat{\boldsymbol{Q}}_3 = \frac{1}{2\sqrt{3}} \begin{pmatrix} 1 \\ -\sqrt{3} \\ 1 \\ \sqrt{3} \\ -2 \\ 0 \end{pmatrix}.$$

The equations $\underline{V} \cdot \hat{\boldsymbol{Q}}_I = \mathbf{0}$ for $I = 1, 2, 3$ are readily verified.
The symmetry reveals that another eigenmode can be read off from Figure 19.4.
This yields the corresponding normalized eigenvector

$$\hat{\boldsymbol{Q}}_4 = \sqrt{m} \begin{pmatrix} {a_{4,1}}^1 \\ {a_{4,1}}^2 \\ {a_{4,2}}^1 \\ {a_{4,2}}^2 \\ {a_{4,3}}^1 \\ {a_{4,3}}^2 \end{pmatrix} = \frac{1}{2\sqrt{3}} \begin{pmatrix} \sqrt{3} \\ 1 \\ -\sqrt{3} \\ 1 \\ 0 \\ -2 \end{pmatrix},$$

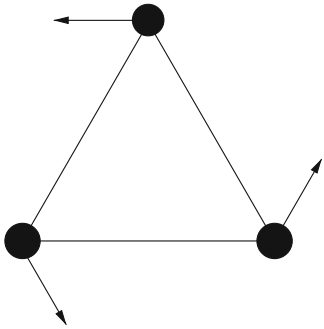


Figure 19.3: The rotation mode $\hat{\boldsymbol{Q}}_3$.

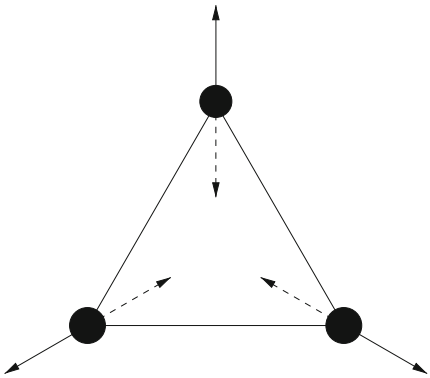


Figure 19.4: The eigenmode $\hat{\boldsymbol{Q}}_4 = \sqrt{m}\hat{\boldsymbol{a}}_4$.

and application of

$$\omega_4^2 \hat{\boldsymbol{Q}}_4 = \frac{1}{m} \underline{V} \cdot \hat{\boldsymbol{Q}}_4,$$

yields for the corresponding frequency

$$\omega_4^2 = \frac{3K}{m}.$$

So far we have found four eigenmodes of the planar system, and there must still be two remaining eigenmodes, which must be orthogonal on the eigenmodes $\hat{\boldsymbol{Q}}_1, \ldots \hat{\boldsymbol{Q}}_4$. This yields for

$$\hat{\boldsymbol{Q}}_I = \sqrt{m} \begin{pmatrix} {a_{I,1}}^1 \\ {a_{I,1}}^2 \\ {a_{I,2}}^1 \\ {a_{I,2}}^2 \\ {a_{I,3}}^1 \\ {a_{I,3}}^2 \end{pmatrix}, \quad I = 5, 6$$

the conditions

$$\sqrt{3}({a_{I,1}}^1 - {a_{I,2}}^1) + {a_{I,1}}^2 + {a_{I,2}}^2 - 2{a_{I,3}}^2 = 0,$$

$${a_{I,1}}^1 + {a_{I,2}}^1 + {a_{I,3}}^1 = 0,$$

$${a_{I,1}}^2 + {a_{I,2}}^2 + {a_{I,3}}^2 = 0,$$

$${a_{I,1}}^1 + {a_{I,2}}^1 - 2{a_{I,3}}^1 + \sqrt{3}({a_{I,2}}^2 - {a_{I,1}}^2) = 0,$$

with general solutions

$$\hat{\boldsymbol{Q}}_{I=5,6} \sim \frac{A}{2\sqrt{3}} \begin{pmatrix} \sqrt{3} \\ -1 \\ -\sqrt{3} \\ -1 \\ 0 \\ 2 \end{pmatrix} + \frac{B}{2\sqrt{3}} \begin{pmatrix} 1 \\ \sqrt{3} \\ 1 \\ -\sqrt{3} \\ -2 \\ 0 \end{pmatrix}.$$

Application of $\underline{\Omega^2}$ reveals that these are degenerate eigenvectors with eigenvalue

$$\omega_5^2 = \omega_6^2 = \frac{3K}{2m},$$

and an orthonormal basis in the degeneracy subspace is provided by

$$\hat{\boldsymbol{Q}}_5 = \frac{1}{2\sqrt{3}} \begin{pmatrix} \sqrt{3} \\ -1 \\ -\sqrt{3} \\ -1 \\ 0 \\ 2 \end{pmatrix}, \quad \hat{\boldsymbol{Q}}_6 = \frac{1}{2\sqrt{3}} \begin{pmatrix} 1 \\ \sqrt{3} \\ 1 \\ -\sqrt{3} \\ -2 \\ 0 \end{pmatrix}.$$

The corresponding eigenmodes are shown in Figure 19.5.
The general small oscillation with $\omega > 0$ is then given by

$$\begin{pmatrix} {x_1}^1(t) \\ {x_1}^2(t) \\ {x_2}^1(t) \\ {x_2}^2(t) \\ {x_3}^1(t) \\ {x_3}^2(t) \end{pmatrix} = \sum_{I=4}^{6} \hat{\boldsymbol{Q}}_I x_I(t)$$

with

$$x_I(t) = x_I(0)\cos(\omega_I t) + \frac{\dot{x}_I(0)}{\omega_I}\sin(\omega_I t).$$

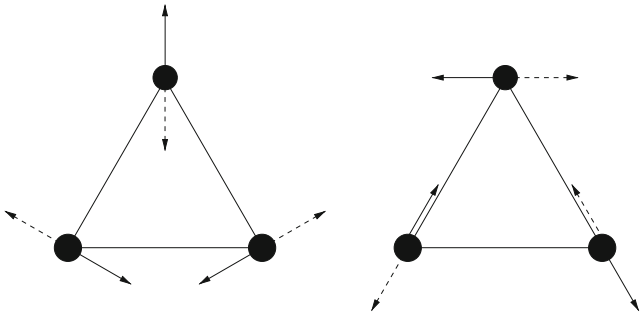


Figure 19.5: The eigenmodes $\hat{\boldsymbol{Q}}_5$ and $\hat{\boldsymbol{Q}}_6$.

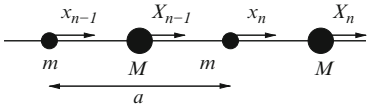


Figure 19.6: A diatomic linear chain with masses m and M and lattice constant a.

The diatomic linear chain

Lines of harmonically bound atoms provide important model systems for oscillations in solid state physics. We consider in particular a diatomic chain of $2N$ atoms with masses m and M, respectively see Figure 19.6. The force constant between the atoms is K and their equilibrium distance is $a/2$. The number N of atom pairs is assumed to be even for simplicity.
We label the pairs of atoms with an index n, $1-(N/2) \leq n \leq N/2$, and we use periodic boundary conditions for the displadements x_n and X_n,

$$x_{n+N} = x_n, \quad X_{n+N} = X_n.$$

The Lagrange function

$$L = \sum_{n=1-(N/2)}^{N/2} \left(\frac{m}{2}\dot{x}_n^2 + \frac{M}{2}\dot{X}_n^2 - \frac{K}{2}(X_n - x_n)^2 - \frac{K}{2}(x_n - X_{n-1})^2 \right)$$

yields equations of motion

$$m\ddot{x}_n = -K(2x_n - X_n - X_{n-1}), \quad M\ddot{X}_n = -K(2X_n - x_n - x_{n+1}), \tag{19.70}$$

which can be solved using Fourier decomposition on a finite periodic chain,

$$x_n(t) = \frac{1}{\sqrt{N}} \sum_k \tilde{q}_k(t) \exp(\mathrm{i}nka), \tag{19.71}$$

$$X_n(t) = \frac{1}{\sqrt{N}} \sum_k \tilde{Q}_k(t) \exp(\mathrm{i}nka),$$

with

$$k = \frac{2\pi\tilde{n}}{Na}, \quad 1 - \frac{N}{2} \leq \tilde{n} \leq \frac{N}{2}.$$

The geometric series

$$\sum_{n=1-(N/2)}^{N/2} \exp\left(2\pi\mathrm{i}n\frac{\tilde{n}-\tilde{m}}{N}\right) = \exp\left[\mathrm{i}\pi\left(\frac{2}{N}-1\right)(\tilde{n}-\tilde{m})\right]$$
$$\times \sum_{n=0}^{N-1} \exp\left(2\pi\mathrm{i}n\frac{\tilde{n}-\tilde{m}}{N}\right) = \exp\left[\mathrm{i}\pi\left(\frac{2}{N}-1\right)(\tilde{n}-\tilde{m})\right]$$
$$\times \frac{1-\exp[2\pi\mathrm{i}(\tilde{n}-\tilde{m})]}{1-\exp\left[\frac{2\pi\mathrm{i}}{N}(\tilde{n}-\tilde{m})\right]} = N\delta_{\tilde{n},\tilde{m}} \tag{19.72}$$

implies that the inversion of (19.71) is

$$\tilde{q}_k(t) = \frac{1}{\sqrt{N}} \sum_{n=1-(N/2)}^{N/2} x_n(t) \exp(-\mathrm{i}nka) = \tilde{q}^+_{-k}(t).$$

Since the resulting system of ordinary differential equations for $\tilde{q}_k(t)$ and $\tilde{Q}_k(t)$ is linear with constant coefficients, we also use Fourier transformation to the frequency domain,

$$\tilde{q}_k(t) = \int d\omega\, \tilde{q}_k(\omega) \exp(-\mathrm{i}\omega t),$$

and the coupled set of equations (19.70) separate into coupled pairs of equations for different wave numbers k,

$$(m\omega^2 - 2K)\tilde{q}_k(\omega) + K(1 + \exp(-\mathrm{i}ka))\tilde{Q}_k(\omega) = 0, \tag{19.73}$$

$$(M\omega^2 - 2K)\tilde{Q}_k(\omega) + K(1 + \exp(\mathrm{i}ka))\tilde{q}_k(\omega) = 0. \tag{19.74}$$

This implies that there is a unique set of frequencies $\omega = \omega_k$ for each wave number k which has to satisfy

$$mM\omega_k^4 - 2K(m+M)\omega_k^2 + 2K^2(1 - \cos(ka)) = 0.$$

This condition has two solutions (up to irrelevant overall signs of $\omega_{k\pm}$),

$$\omega^2_{k\pm} = K\left(\frac{1}{M}+\frac{1}{m}\right) \pm K\sqrt{\frac{1}{M^2}+\frac{1}{m^2}+\frac{2}{mM}\cos(ka)}$$
$$= K\left(\frac{1}{M}+\frac{1}{m}\right) \pm K\sqrt{\left(\frac{1}{M}+\frac{1}{m}\right)^2 - \frac{4}{mM}\sin^2\left(\frac{ka}{2}\right)}, \tag{19.75}$$

and we have

$$\tilde{q}_k(\omega) = \tilde{q}_{k+}\delta(\omega - \omega_{k+}) + \tilde{q}_{k-}\delta(\omega - \omega_{k-}).$$

Equation (19.75) reads in terms of the reduced mass $\mu = mM/(m+M)$ of the atom pair in the unit cell

$$\omega_{k\pm}^2 = \frac{K}{\mu}\left(1 \pm \sqrt{1 - \frac{4\mu}{m+M}\sin^2\left(\frac{ka}{2}\right)}\right). \tag{19.76}$$

An example of these dispersion relations with $M = 1.5m$ is displayed in Figure 19.7.

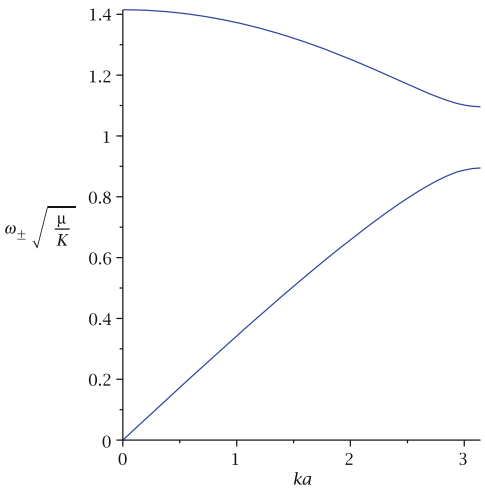


Figure 19.7: The frequencies $\omega_{k\pm}$ from the dispersion relation (19.76) for $M = 1.5m$ and $0 \le ka \le \pi$. The frequencies $\omega_{k\pm}$ are displayed in units of $\sqrt{K/\mu}$, where μ is the reduced mass of the atom pair in a unit cell.

Note that the Lagrange function for a single atom pair in the unit cell is

$$L = \frac{1}{2}(m+M)\dot{R}^2 + \frac{\mu}{2}\dot{r}^2 - \frac{K}{2}r^2, \quad r = x - X, \quad R = \frac{mx + MX}{m+M},$$

and therefore the oscillation frequency of the single pair is $\sqrt{K/\mu}$.
The frequencies at $k = 0$ are $\omega_{0-} = 0$ and

$$\omega_{0+} = \sqrt{\frac{2K}{\mu}}.$$

The solution of (19.73,19.74) for $\omega_{0-} = 0$,

$$\tilde{q}_{0-} = \tilde{Q}_{0-},$$

is a uniform translation of the whole chain,

$$x_n(t) = X_n(t) = \tilde{q}_{0-}/\sqrt{N}.$$

The solution for ω_{0+},

$$m\tilde{q}_{0+} = -M\tilde{Q}_{0+},$$

is an oscillation

$$\begin{pmatrix} x_n(t) \\ X_n(t) \end{pmatrix} = A \begin{pmatrix} M \\ -m \end{pmatrix} \cos\left(\sqrt{\frac{2K}{\mu}}t + \varphi\right).$$

The acoustic solution for $ka = \pi$ is

$$\omega_{(\pi/a)-} = \sqrt{\frac{2K}{M}}, \quad \tilde{q}_{(\pi/a)-} = 0,$$

i.e. only the heavy atoms oscillate,

$$\begin{pmatrix} x_n(t) \\ X_n(t) \end{pmatrix} = (-)^n A \begin{pmatrix} 0 \\ 1 \end{pmatrix} \cos\left(\sqrt{\frac{2K}{M}}t + \varphi\right).$$

On the other hand, the optical eigenmode with $ka = \pi$,

$$\omega_{(\pi/a)+} = \sqrt{\frac{2K}{m}}, \quad \tilde{Q}_{(\pi/a)+} = 0,$$

corresponds to an oscillation of the light atoms,

$$\begin{pmatrix} x_n(t) \\ X_n(t) \end{pmatrix} = (-)^n A \begin{pmatrix} 1 \\ 0 \end{pmatrix} \cos\left(\sqrt{\frac{2K}{m}}t + \varphi\right).$$

The general longitudinal oscillation will be a superposition of all longitudinal eigenvibrations.

Quantization of N-particle oscillations

The Lagrange function (19.56) implies canonical commutation relations

$$[x_i{}^k(t), \dot{x}_j{}^l(t)] = \frac{\mathrm{i}\hbar}{m_i}\delta_{ij}\delta^{kl}, \quad [x_i{}^k(t), x_j{}^l(t)] = 0, \quad [\dot{x}_i{}^k(t), \dot{x}_j{}^l(t)] = 0.$$

This yields commutation relations for the normal coordinates

$$[q_I, q_J] = 0, \quad [q_I, q_J^+] = \frac{\hbar}{2\omega_I}\delta_{IJ}.$$

Therefore we find canonical annihilation and creation operators for the eigenvibrations in the form

$$a_I = \sqrt{\frac{2\omega_I}{\hbar}} q_I, \quad a_I^+ = \sqrt{\frac{2\omega_I}{\hbar}} q_I^+.$$

The discussion of the diatomic chain taught us that for lattice oscillations the eigenmodes also depend on wave vectors in a Brillouin zone, and the following section will show that there can be up to $3N$ branches if we have N atoms per unit cell. Therefore we will have annihilation and creation operators for lattice vibrations which are related to the corresponding normal modes through

$$a_I(\boldsymbol{k}) = \sqrt{\frac{2\omega_{I,\boldsymbol{k}}}{\hbar}} q_I(\boldsymbol{k}), \quad a_I^+(\boldsymbol{k}) = \sqrt{\frac{2\omega_{I,\boldsymbol{k}}}{\hbar}} q_I^+(\boldsymbol{k}).$$

The elementary excitations $a_I^+(\boldsymbol{k})|0\rangle$ of the lattice vibrations are denoted as *phonons*.

19.6 Quantized lattice vibrations – phonons

We will first generalize the previous discussion of vibrations in N-particle systems to the case of three-dimensional lattices, and then quantize the lattice vibrations

We denote the three basis vectors of a three-dimensional lattice with $\boldsymbol{a}_i$, $1 \leq i \leq 3$. Each location $\boldsymbol{\ell} = n^i \boldsymbol{a}_i$ in the lattice denotes a particular location of a corresponding unit cell, and we can use $\boldsymbol{\ell}$ or equivalently the three integers n^i also to address the particular unit cell to which the point $\boldsymbol{\ell}$ belongs. Suppose we have N atoms (or ions) per unit cell in the lattice. We denote the displacement of the A-th atom from its equilibrium value in cell $\boldsymbol{\ell}$ by $\boldsymbol{x}_{\boldsymbol{\ell},A}(t)$, and in the harmonic approximation the displacements satisfy equations of motion

$$m_A \ddot{\boldsymbol{x}}_{\boldsymbol{\ell},A} + \sum_{\boldsymbol{\ell}',A'} \underline{V}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'} \cdot \boldsymbol{x}_{\boldsymbol{\ell}',A'} = \boldsymbol{0}, \tag{19.77}$$

corresponding to a Lagrange function

$$L = \frac{1}{2} \sum_{\boldsymbol{\ell},A} m_A \dot{\boldsymbol{x}}_{\boldsymbol{\ell},A}^2 - \frac{1}{2} \sum_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'} \boldsymbol{x}_{\boldsymbol{\ell},A} \cdot \underline{V}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'} \cdot \boldsymbol{x}_{\boldsymbol{\ell}',A'}. \tag{19.78}$$

Substitution of Fourier transforms

$$\boldsymbol{x}_{\boldsymbol{\ell},A}(t) = \frac{1}{\sqrt{m_A}} \int d\omega \, \boldsymbol{Q}_{\boldsymbol{\ell},A}(\omega) \exp(-\mathrm{i}\omega t)$$

into the equations of motion (19.77) yields the eigenvalue conditions

$$\sum_{\boldsymbol{\ell}',A'} \underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'} \cdot \boldsymbol{Q}_{\boldsymbol{\ell}',A'}(\omega) = \omega^2 \boldsymbol{Q}_{\boldsymbol{\ell},A}(\omega) \tag{19.79}$$

with the symmetric matrices

$$\underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B} = \frac{1}{\sqrt{m_A m_B}} \underline{V}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B} = \underline{\Omega^2}^T_{\boldsymbol{\ell}',B;\boldsymbol{\ell},A}. \tag{19.80}$$

Translation invariance in the lattice implies that $\underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B}$ cannot depend on $\boldsymbol{\ell}+\boldsymbol{\ell}'$. Therefore we can write

$$\underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B} = \underline{\Omega^2}_{A,B}(\boldsymbol{\ell}-\boldsymbol{\ell}') = \frac{V}{(2\pi)^3}\int_{\mathcal{B}} d^3\boldsymbol{k}\, \underline{\tilde{\Omega}^2}_{A,B}(\boldsymbol{k}) \exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{\ell}-\boldsymbol{\ell}')], \tag{19.81}$$

with inversion

$$\underline{\tilde{\Omega}^2}_{A,B}(\boldsymbol{k}) = \sum_{\boldsymbol{\ell}} \underline{\Omega^2}_{A,B}(\boldsymbol{\ell}) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}).$$

Symmetry of the real matrix $\underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',B}$ under $i,\boldsymbol{\ell},A \leftrightarrow j,\boldsymbol{\ell}',B$ implies

$$\begin{aligned}
\tilde{\Omega}^2_{iA,jB}(\boldsymbol{k}) &= \sum_{\boldsymbol{\ell}} \Omega^2_{iA,jB}(\boldsymbol{\ell}) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}) = \sum_{\boldsymbol{\ell}} \Omega^2_{jB,iA}(-\boldsymbol{\ell}) \exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}) \\
&= \sum_{\boldsymbol{\ell}} \Omega^2_{jB,iA}(\boldsymbol{\ell}) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}) = \tilde{\Omega}^{2,*}_{jB,iA}(\boldsymbol{k}) = \tilde{\Omega}^{2,+}_{iA,jB}(\boldsymbol{k}) \\
&= \tilde{\Omega}^2_{jB,iA}(-\boldsymbol{k}),
\end{aligned}$$

i.e.

$$\underline{\tilde{\Omega}^2}(\boldsymbol{k}) = \underline{\tilde{\Omega}^2}^+(\boldsymbol{k}) = \underline{\tilde{\Omega}^2}^T(-\boldsymbol{k}). \tag{19.82}$$

Substitution of (19.81) and

$$\boldsymbol{Q}_{\boldsymbol{\ell},A}(\omega) = \frac{V}{(2\pi)^3}\int_{\mathcal{B}} d^3\boldsymbol{k}\, \tilde{\boldsymbol{Q}}_{\boldsymbol{k},A}(\omega) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}).$$

in (19.79) yields,

$$\sum_B \underline{\tilde{\Omega}^2}_{A,B}(\boldsymbol{k})\cdot\tilde{\boldsymbol{Q}}_{\boldsymbol{k},B}(\omega) = \omega^2 \tilde{\boldsymbol{Q}}_{\boldsymbol{k},A}(\omega). \tag{19.83}$$

For fixed value of $\boldsymbol{k}$, this is a hermitian eigenvalue problem for the $3N$-dimensional complex vector

$$\tilde{\boldsymbol{Q}}_{\boldsymbol{k}}(\omega) = \{\tilde{Q}^i_{\boldsymbol{k},A}(\omega)\}, \quad 1 \le i \le 3, \quad 1 \le A \le N.$$

Reality of the displacement vectors $\boldsymbol{x}_{\boldsymbol{\ell},A}(t)$ implies $\boldsymbol{Q}_{\boldsymbol{\ell},A}(\omega) = \boldsymbol{Q}^+_{\boldsymbol{\ell},A}(-\omega)$ and

$$\tilde{\boldsymbol{Q}}^+_{\boldsymbol{k}}(\omega) = \tilde{\boldsymbol{Q}}_{-\boldsymbol{k}}(-\omega).$$

For each point $\boldsymbol{k}$ in the Brillouin zone, there will be $3N$ solutions $\omega^2_I(\boldsymbol{k})$ and $\hat{\boldsymbol{Q}}_I(\boldsymbol{k})$ of (19.83) which satisfy the orthogonality property

$$\begin{aligned}
\hat{\boldsymbol{Q}}^+_I(\boldsymbol{k})\cdot\hat{\boldsymbol{Q}}_J(\boldsymbol{k}) &\equiv \sum_A \hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{k})\cdot\hat{\boldsymbol{Q}}_{J,A}(\boldsymbol{k}) \equiv \sum_{i,A} \hat{Q}^{i+}_{I,A}(\boldsymbol{k})\hat{Q}^i_{J,A}(\boldsymbol{k}) \\
&= \delta_{IJ}.
\end{aligned} \tag{19.84}$$

The hermiticity and transposition properties imply that we have as a concequence of (19.83) for the normalized solutions,

$$\sum_B \underline{\tilde{\Omega}^2}_{A,B}(\boldsymbol{k}) \cdot \hat{\boldsymbol{Q}}_{I,B}(\boldsymbol{k}) = \omega_I^2(\boldsymbol{k}) \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}), \tag{19.85}$$

also the equations

$$\sum_B \underline{\tilde{\Omega}^2}_{A,B}(-\boldsymbol{k}) \cdot \hat{\boldsymbol{Q}}^+_{I,B}(\boldsymbol{k}) = \omega_I^2(\boldsymbol{k}) \hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{k}) \tag{19.86}$$

and

$$\sum_A \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}) \cdot \underline{\tilde{\Omega}^2}_{A,B}(-\boldsymbol{k}) = \omega_I^2(\boldsymbol{k}) \hat{\boldsymbol{Q}}_{I,B}(\boldsymbol{k}). \tag{19.87}$$

Up to linear combinations within degeneracy subspaces, the general set of solutions of the conditions (19.83) will then have the form

$$\tilde{\boldsymbol{Q}}_{\boldsymbol{k}}(\omega) = \sum_I \Big(q_I(\boldsymbol{k}) \hat{\boldsymbol{Q}}_I(\boldsymbol{k}) \delta(\omega - \omega_I(\boldsymbol{k})) + q_I^+(-\boldsymbol{k}) \hat{\boldsymbol{Q}}_I^+(-\boldsymbol{k}) \delta(\omega + \omega_I(-\boldsymbol{k})) \Big)$$

with complex factors $q_I(\boldsymbol{k})$. This yields the general lattice vibration in terms of the orthonormalized solutions of (19.83),

$$\begin{aligned} \boldsymbol{x}_{\boldsymbol{\ell},A}(t) = \frac{V}{(2\pi)^3 \sqrt{m_A}} \int_{\mathcal{B}} d^3\boldsymbol{k} \sum_I \Big[& q_I(\boldsymbol{k}) \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}) \exp\Big(\mathrm{i}[\boldsymbol{k} \cdot \boldsymbol{\ell} - \omega_I(\boldsymbol{k}) t] \Big) \\ & + q_I^+(\boldsymbol{k}) \hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{k}) \exp\Big(- \mathrm{i}[\boldsymbol{k} \cdot \boldsymbol{\ell} - \omega_I(\boldsymbol{k}) t] \Big) \Big], \end{aligned} \tag{19.88}$$

$$\begin{aligned} \dot{\boldsymbol{x}}_{\boldsymbol{\ell},A}(t) = \int_{\mathcal{B}} d^3\boldsymbol{k} \sum_I \frac{-\mathrm{i}\omega_I(\boldsymbol{k}) V}{(2\pi)^3 \sqrt{m_A}} \Big[& q_I(\boldsymbol{k}) \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}) \exp\Big(\mathrm{i}[\boldsymbol{k} \cdot \boldsymbol{\ell} - \omega_I(\boldsymbol{k}) t] \Big) \\ & - q_I^+(\boldsymbol{k}) \hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{k}) \exp\Big(- \mathrm{i}[\boldsymbol{k} \cdot \boldsymbol{\ell} - \omega_I(\boldsymbol{k}) t] \Big) \Big], \end{aligned} \tag{19.89}$$

$$\begin{aligned} q_I(\boldsymbol{k}) = \frac{1}{2} \sum_{\boldsymbol{\ell},A} & \exp\Big(- \mathrm{i}[\boldsymbol{k} \cdot \boldsymbol{\ell} - \omega_I(\boldsymbol{k}) t] \Big) \sqrt{m_A} \\ & \times \hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{k}) \cdot \Big(\boldsymbol{x}_{\boldsymbol{\ell},A}(t) + \frac{\mathrm{i}}{\omega_I(\boldsymbol{k})} \dot{\boldsymbol{x}}_{\boldsymbol{\ell},A}(t) \Big). \end{aligned} \tag{19.90}$$

The dual orthogonality relation to (19.84) follows from re-substitution of $q_I(\boldsymbol{k})$ into (19.88),

$$\frac{V}{(2\pi)^3} \int_{\mathcal{B}} d^3\boldsymbol{k} \sum_I \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}) \otimes \hat{\boldsymbol{Q}}^+_{I,B}(\boldsymbol{k}) \exp[\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{\ell} - \boldsymbol{\ell}')] = \delta_{AB} \delta_{\boldsymbol{\ell},\boldsymbol{\ell}'} \underline{1}. \tag{19.91}$$

This is actually fulfilled due to two more fundamental completeness relations. The first relation is completeness of $3N$ orthonormal unit vectors $\hat{\boldsymbol{Q}}_I(\boldsymbol{k}) \equiv \{\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\}_{1\leq A\leq N}$ in a $3N$-dimensional vector space,

$$\sum_I \hat{\boldsymbol{Q}}_I(\boldsymbol{k}) \otimes \hat{\boldsymbol{Q}}_I^+(\boldsymbol{k}) = \underline{1},$$

where $\underline{1}$ is the $3N \times 3N$ unit matrix, or if the atomic indices are spelled out,

$$\sum_I \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k}) \otimes \hat{\boldsymbol{Q}}_{I,B}^+(\boldsymbol{k}) = \delta_{AB}\underline{1}, \tag{19.92}$$

where now $\underline{1}$ is the 3×3 unit matrix refering to the spatial indices. The second relation is the completeness relation (19.36).
The canonical quantization relations

$$[\boldsymbol{x}_{\boldsymbol{\ell},A}(t) \overset{\otimes}{,} \dot{\boldsymbol{x}}_{\boldsymbol{\ell}',B}(t)] = \frac{\mathrm{i}\hbar}{m_A}\delta_{AB}\delta_{\boldsymbol{\ell},\boldsymbol{\ell}'}\underline{1},$$

$$[\boldsymbol{x}_{\boldsymbol{\ell},A}(t) \overset{\otimes}{,} \boldsymbol{x}_{\boldsymbol{\ell}',B}(t)] = 0, \quad [\dot{\boldsymbol{x}}_{\boldsymbol{\ell},A}(t) \overset{\otimes}{,} \dot{\boldsymbol{x}}_{\boldsymbol{\ell}',B}(t)] = 0,$$

imply

$$[q_I(\boldsymbol{k}), q_J(\boldsymbol{k}')] = 0, \quad [q_I(\boldsymbol{k}), q_J^+(\boldsymbol{k}')] = \frac{\hbar}{2\omega_I(\boldsymbol{k})}\frac{(2\pi)^3}{V}\delta_{IJ}\delta(\boldsymbol{k}-\boldsymbol{k}'),$$

i.e. the phonon annihilation operator for the Ith mode with wave vector $\boldsymbol{k}$ in the lattice is

$$a_I(\boldsymbol{k}) = \frac{1}{2}\sqrt{\frac{\omega_I(\boldsymbol{k})V}{\pi^3\hbar}}q_I(\boldsymbol{k}), \tag{19.93}$$

and the displacement operators in terms of the phonon operators are given by

$$\boldsymbol{x}_{\boldsymbol{\ell},A}(t) = \sum_I \boldsymbol{x}_{I,\boldsymbol{\ell},A}(t), \tag{19.94}$$

$$\begin{aligned}\boldsymbol{x}_{I,\boldsymbol{\ell},A}(t) = \sqrt{\frac{\hbar V}{(2\pi)^3 m_A}}\int_{\mathcal{B}}\frac{d^3\boldsymbol{k}}{\sqrt{2\omega_I(\boldsymbol{k})}}\Big[a_I(\boldsymbol{k})\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\exp\Big(\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{\ell}-\omega_I(\boldsymbol{k})t]\Big)\\ +a_I^+(\boldsymbol{k})\hat{\boldsymbol{Q}}_{I,A}^+(\boldsymbol{k})\exp\Big(-\mathrm{i}[\boldsymbol{k}\cdot\boldsymbol{\ell}-\omega_I(\boldsymbol{k})t]\Big)\Big].\end{aligned} \tag{19.95}$$

The Lagrange function (19.78) implies a Hamiltonian for the lattice vibrations,

$$H = \frac{1}{2}\sum_{\boldsymbol{\ell},A} m_A\dot{\boldsymbol{x}}_{\boldsymbol{\ell},A}^2 + \frac{1}{2}\sum_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'}\sqrt{m_A m_{A'}}\boldsymbol{x}_{\boldsymbol{\ell},A}\cdot\underline{\Omega^2}_{\boldsymbol{\ell},A;\boldsymbol{\ell}',A'}\cdot\boldsymbol{x}_{\boldsymbol{\ell}',A'}.$$

This yields after substitution of equations (19.94,19.95) and use of the eigenvalue, hermiticity and orthogonality conditions for the eigenvalue problem (19.85-19.87) the result[13]

$$H = \int_{\mathcal{B}} d^3\boldsymbol{k} \sum_I \hbar\omega_I(\boldsymbol{k}) a_I^+(\boldsymbol{k}) a_I(\boldsymbol{k}). \tag{19.96}$$

It is uncommon but helpful for a better understanding of Bloch and Wannier states of electrons to point out an analogy with lattice vibrations at this point. We have seen in Sections 10.1, 10.2 and 10.3 that electrons in lattices can be described in terms of delocalized Bloch states $\psi_n(k,x,t) = \psi_n(k,x)\exp(-\mathrm{i}\omega_n(k)t)$ or corresponding Wannier states $w_{n,\nu}(x)$, $w_{n,\nu}(x,t)$. Here ν labelled the different cells in the lattice and n labelled the different electron energy bands in the periodic potential of the crystal. We have encountered the corresponding states in three-dimensional lattices in equations (19.43,19.46). To make the connection to lattice vibrations, we re-express the result (19.88) for the particular phonon energy band I in the form

$$\boldsymbol{x}_{I,\boldsymbol{\ell},A}(t) = \frac{V}{(2\pi)^3}\int d^3\boldsymbol{k}\, \tilde{\boldsymbol{x}}_{I,\boldsymbol{k},A}(t)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}),$$

$$\begin{aligned}\tilde{\boldsymbol{x}}_{I,\boldsymbol{k},A}(t) &= \sum_{\boldsymbol{\ell}} \boldsymbol{x}_{I,\boldsymbol{\ell},A}(t)\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{\ell}) = \tilde{\boldsymbol{x}}^+_{I,-\boldsymbol{k},A}(t)\\ &= \frac{q_I(\boldsymbol{k})}{\sqrt{m_A}}\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\exp[-\mathrm{i}\omega_I(\boldsymbol{k})t]\\ &\quad + \frac{q_I^+(-\boldsymbol{k})}{\sqrt{m_A}}\hat{\boldsymbol{Q}}^+_{I,A}(-\boldsymbol{k})\exp[\mathrm{i}\omega_I(-\boldsymbol{k})t].\end{aligned}$$

Instead of the continuous dependence of the Bloch or Wannier type wave functions $\phi_n(\boldsymbol{k},\boldsymbol{x},t) \sim \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})u_n(\boldsymbol{k},\boldsymbol{x},t)$ and $w_n(\boldsymbol{\ell},\boldsymbol{x},t)$ on location $\boldsymbol{x}$, we have displacement variables at the discrete locations $\{\boldsymbol{\ell},A\}$ in the lattice. However with the correspondence of band indices $n \leftrightarrow I$, the Brillouin zone representation $\tilde{\boldsymbol{x}}_{I,\boldsymbol{k},A}(t)$ of the displacements corresponds to the Bloch waves (19.43) for electron states, while the set of displacements $\{\boldsymbol{x}_{I,\boldsymbol{\ell},A}(t)\}_{1\le A\le N}$ in the unit cell at $\boldsymbol{\ell}$ corresponds to the Wannier states (19.46).

19.7 Electron-phonon interactions

Phonons in the lattice of a solid material naturally couple to electrons through the electrostatic interaction between the electrons and the ion cores. If we neglect electron-electron interactions, the basic Schrödinger picture Hamiltonian

[13] You also have to use that the matrix $\underline{\tilde{\Omega}^2}(\boldsymbol{k})$ has a positive semi-definite square root $\underline{\tilde{\Omega}}(\boldsymbol{k})$, see Problem 2. Therefore we also have e.g.

$$\sum_{A,B}\hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\cdot\underline{\tilde{\Omega}^2}_{A,B}(-\boldsymbol{k})\cdot\hat{\boldsymbol{Q}}_{J,B}(-\boldsymbol{k}) = \omega_I(\boldsymbol{k})\omega_J(-\boldsymbol{k})\sum_A \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{k})\hat{\boldsymbol{Q}}_{J,A}(-\boldsymbol{k}).$$

for quantized electrons in a lattice of ion cores with N atoms in the unit cell has the form

$$H = -\int d^3\boldsymbol{x} \sum_\sigma \psi_\sigma^+(\boldsymbol{x}) \left(\frac{\hbar^2}{2m}\Delta + \sum_{\boldsymbol{\ell},A} \frac{n_A e^2}{4\pi\epsilon_0 \, |\boldsymbol{x} - \boldsymbol{r}_{\boldsymbol{\ell},A}|} \right) \psi_\sigma(\boldsymbol{x}).$$

We assume that the A-th atom or ion in the unit cell couples to the electron with an effective charge $n_A e$, and we treat the atoms or ions as classical sources of electrostatic fields. However, we treat the lattice vibrations on the quantum level, which according to Sections 19.5 and 19.6 amounts to canonical quantization of the lattice displacements

$$\boldsymbol{x}_{\boldsymbol{\ell},A} = \boldsymbol{r}_{\boldsymbol{\ell},A} - \boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A}.$$

The leading order expansion of the Coulomb term

$$\frac{n_A e}{|\boldsymbol{x} - \boldsymbol{r}_{\boldsymbol{\ell},A}|} \simeq \frac{n_A e}{|\boldsymbol{x} - \boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A}|} + n_A e \frac{(\boldsymbol{x} - \boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A}) \cdot \boldsymbol{x}_{\boldsymbol{\ell},A}}{|\boldsymbol{x} - \boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A}|^3} \tag{19.97}$$

corresponds to a dipole approximation in the language of Chapter 15, except that here the dipole operator $\boldsymbol{d}_{\boldsymbol{\ell},A} = n_A e \boldsymbol{x}_{\boldsymbol{\ell},A}$ is quantized according to (19.94,19.95). This yields an electron-phonon interaction Hamiltonian of the form

$$H_{e-q} = -\sqrt{\frac{\hbar V}{(2\pi)^3}} \int d^3\boldsymbol{x} \sum_{\sigma,I,\boldsymbol{\ell},A} \psi_\sigma^+(\boldsymbol{x}) \psi_\sigma(\boldsymbol{x}) \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{\sqrt{2\omega_I(\boldsymbol{q})}} \frac{e}{\sqrt{m_A}}$$
$$\boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x}) \cdot \left[a_I(\boldsymbol{q}) \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{q}) \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{\ell}) + a_I^+(\boldsymbol{q}) \hat{\boldsymbol{Q}}^+_{I,A}(\boldsymbol{q}) \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{\ell}) \right],$$

where we substituted the time-independent phonon operators $\boldsymbol{x}_{\boldsymbol{\ell},A}(0)$ for the Hamiltonian in the Schrödinger picture. For the electron operators, we could substitute Bloch or Wannier type operators. However, Bloch operators make much more sense, because the dipole approximation (19.97) is a small oscillation approximation in the sense $|\boldsymbol{x}_{\boldsymbol{\ell},A}| \ll |\boldsymbol{x} - \boldsymbol{x}^{(0)}_{\boldsymbol{\ell},A}|$, or otherwise we should include quadrupole and higher order terms. This implies that matrix elements of electron states with the lattice electric fields $\boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x})$ must not be dominated by large terms from the ion cores. The linear phonon coupling Hamiltonian H_{e-q} should therefore not be a good approximation for the localized electrons in Wannier states. Evaluation of the substitution of the free electron operators through Bloch operators (19.41) in H_{e-q} uses the fact that integration over $\boldsymbol{x}$ can be split into summation over the lattice $\boldsymbol{l}$ and integration over the unit lattice cell V,

$$\int d^3\boldsymbol{x} \, f(\boldsymbol{x}) = \sum_{\boldsymbol{l}} \int_V d^3\boldsymbol{x} \, f(\boldsymbol{l} + \boldsymbol{x}),$$

and that the lattice electric fields satisfy

$$\boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x}) = \boldsymbol{E}_{\boldsymbol{0},A}(\boldsymbol{x}-\boldsymbol{\ell}).$$

We denote the Bloch operators for the electrons by $c_{n,\sigma}(\boldsymbol{k})$ to avoid confusion with the phonon operators. This yields the following form for the electron-phonon interaction operator,

$$\begin{aligned} H_{e-q} = -\sqrt{\frac{\hbar V}{(2\pi)^3}} \sum_{\sigma,I,\boldsymbol{\ell},A,n,n'} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{\sqrt{2\omega_I(\boldsymbol{q})}} \int_{\mathcal{B}} d^3\boldsymbol{k} \int_V d^3\boldsymbol{x} \frac{e}{\sqrt{m_A}} \\ \boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x}) \cdot \Big[u_n^+(\boldsymbol{k}+\boldsymbol{q},\boldsymbol{x}) c_{n,\sigma}^+(\boldsymbol{k}+\boldsymbol{q}) a_I(\boldsymbol{q}) \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{q}) \exp[\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{\ell}-\boldsymbol{x})] \\ + u_n^+(\boldsymbol{k}-\boldsymbol{q},\boldsymbol{x}) c_{n,\sigma}^+(\boldsymbol{k}-\boldsymbol{q}) a_I^+(\boldsymbol{q}) \hat{\boldsymbol{Q}}_{I,A}^+(\boldsymbol{q}) \exp[\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{x}-\boldsymbol{\ell})] \Big] \\ \times c_{n',\sigma}(\boldsymbol{k}) u_{n'}(\boldsymbol{k},\boldsymbol{x}). \end{aligned} \tag{19.98}$$

We can also write this as

$$\begin{aligned} H_{e-q} = \sum_{\sigma,I} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{\sqrt{2\omega_I(\boldsymbol{q})}} \int_{\mathcal{B}} d^3\boldsymbol{k} \left[c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) \cdot \underline{U}_I(\boldsymbol{k},\boldsymbol{q}) \cdot c_\sigma(\boldsymbol{k}) a_I(\boldsymbol{q}) \right. \\ \left. + a_I^+(\boldsymbol{q}) c_\sigma^+(\boldsymbol{k}) \cdot \underline{U}_I^+(\boldsymbol{k},\boldsymbol{q}) \cdot c_\sigma(\boldsymbol{k}+\boldsymbol{q}) \right], \end{aligned} \tag{19.99}$$

with coupling matrices between the phonons and the Bloch electrons,

$$\begin{aligned} U_{I,n,n'}(\boldsymbol{k},\boldsymbol{q}) = -\sqrt{\frac{\hbar V}{(2\pi)^3}} \int_V d^3\boldsymbol{x} \sum_{\boldsymbol{\ell},A} \frac{e}{\sqrt{m_A}} \exp[\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{\ell}-\boldsymbol{x})] \\ \times u_n^+(\boldsymbol{k}+\boldsymbol{q},\boldsymbol{x}) \boldsymbol{E}_{\boldsymbol{\ell},A}(\boldsymbol{x}) \cdot \hat{\boldsymbol{Q}}_{I,A}(\boldsymbol{q}) u_{n'}(\boldsymbol{k},\boldsymbol{x}). \end{aligned} \tag{19.100}$$

The products in (19.99) contain summations over the electron energy band indices n, n'.

Below we will need the following property of the electron-phonon coupling functions,

$$U_{I,n,n'}(\boldsymbol{k}+\boldsymbol{q},-\boldsymbol{q}) = U_{I,n',n}^+(\boldsymbol{k},\boldsymbol{q}). \tag{19.101}$$

The full Hamiltonian also contains the free Hamiltonian for the phonons and the Bloch electrons

$$H_0 = \int_{\mathcal{B}} d^3\boldsymbol{k} \left(\sum_I \hbar\omega_I(\boldsymbol{k}) a_I^+(\boldsymbol{k}) a_I(\boldsymbol{k}) + \sum_\sigma c_\sigma^+(\boldsymbol{k}) \cdot \underline{E}(\boldsymbol{k}) \cdot c_\sigma(\boldsymbol{k}) \right)$$

with

$$\begin{aligned} E_{n,n'}(\boldsymbol{k}) = \frac{\hbar^2}{2m} \left(\int_V d^3\boldsymbol{x}\, \boldsymbol{\nabla} u_n^+(\boldsymbol{k},\boldsymbol{x}) \cdot \boldsymbol{\nabla} u_{n'}(\boldsymbol{k},\boldsymbol{x}) \right. \\ \left. -\mathrm{i}\boldsymbol{k} \cdot \int_V d^3\boldsymbol{x}\, u_n^+(\boldsymbol{k},\boldsymbol{x}) \overleftrightarrow{\boldsymbol{\nabla}} u_{n'}(\boldsymbol{k},\boldsymbol{x}) + \boldsymbol{k}^2 \delta_{n,n'} \right). \end{aligned} \tag{19.102}$$

The two interaction terms in (19.99) describe absorption and emission of a phonon of wave number $\boldsymbol{q}$ by a Bloch electron. The resulting exchange of virtual phonons between electron pairs will generate an effective interaction between the electrons. If interband couplings can be neglected, $U_{I,n,n'}(\boldsymbol{k},\boldsymbol{q}) \propto \delta_{n,n'}$ and $E_{n,n'}(\boldsymbol{k}) \propto \delta_{n,n'}$, a simple method to estimate this phonon mediated electron-electron interaction eliminates the first order phonon coupling through the Lemma 1 (6.16) for exponentials of operators. A unitary transformation $|\Phi\rangle \to |\Phi'\rangle = \exp(A)|\Phi\rangle$ with

$$A = \sum_{\sigma,I} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{\sqrt{2\omega_I(\boldsymbol{q})}} \int_{\mathcal{B}} d^3\boldsymbol{k}\, \frac{1}{E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k}) - \hbar\omega_I(\boldsymbol{q})} \times \left[a_I^+(\boldsymbol{q}) c_\sigma^+(\boldsymbol{k}) U_I^+(\boldsymbol{k},\boldsymbol{q}) c_\sigma(\boldsymbol{k}+\boldsymbol{q}) - c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) U_I(\boldsymbol{k},\boldsymbol{q}) c_\sigma(\boldsymbol{k}) a_I(\boldsymbol{q})\right]$$

eliminates the leading order electron-phonon coupling term due to

$$[A, H_0] + H_{e-q} = 0,$$

and generates a direct electron-electron coupling term

$$\begin{aligned} H_{e-e}^{(q)} &= \left[\frac{1}{2}\,^2[A,H_0] + [A,H_{e-q}]\right]_{c^+c^+cc} = \frac{1}{2}[A,H_{e-q}]\Big|_{c^+c^+cc} \\ &= \sum_{\sigma,\sigma',I} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{4\omega_I(\boldsymbol{q})} \int_{\mathcal{B}} d^3\boldsymbol{k} \int_{\mathcal{B}} d^3\boldsymbol{k}'\, \frac{1}{E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k}) - \hbar\omega_I(\boldsymbol{q})} \\ &\quad \times \left[c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) c_{\sigma'}^+(\boldsymbol{k}') U_I^+(\boldsymbol{k}',\boldsymbol{q}) U_I(\boldsymbol{k},\boldsymbol{q}) c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q}) c_\sigma(\boldsymbol{k})\right. \\ &\quad \left. + c_\sigma^+(\boldsymbol{k}) c_{\sigma'}^+(\boldsymbol{k}'+\boldsymbol{q}) U_I^+(\boldsymbol{k},\boldsymbol{q}) U_I(\boldsymbol{k}',\boldsymbol{q}) c_{\sigma'}(\boldsymbol{k}') c_\sigma(\boldsymbol{k}+\boldsymbol{q})\right]. \end{aligned}$$

In the next step we substitute

$$\boldsymbol{k} \to \boldsymbol{k}+\boldsymbol{q}, \quad \boldsymbol{k}' \to \boldsymbol{k}'+\boldsymbol{q}, \quad \boldsymbol{q} \to -\boldsymbol{q},$$

in the second term in $H_{e-e}^{(q)}$ and use the properties (19.101) and $\omega_I(\boldsymbol{q}) = \omega_I(-\boldsymbol{q})$. This yields

$$\begin{aligned} H_{e-e}^{(q)} &= \sum_{\sigma,\sigma',I} \int_{\mathcal{B}} \frac{d^3\boldsymbol{q}}{4\omega_I(\boldsymbol{q})} \int_{\mathcal{B}} d^3\boldsymbol{k} \int_{\mathcal{B}} d^3\boldsymbol{k}'\, c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) c_{\sigma'}^+(\boldsymbol{k}') U_I^+(\boldsymbol{k}',\boldsymbol{q}) \\ &\quad \times U_I(\boldsymbol{k},\boldsymbol{q}) c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q}) c_\sigma(\boldsymbol{k}) \\ &\quad \times \left[\frac{1}{E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k}) - \hbar\omega_I(\boldsymbol{q})} - \frac{1}{E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k}) + \hbar\omega_I(\boldsymbol{q})}\right] \\ &= \frac{\hbar}{2} \sum_{\sigma,\sigma',I} \int_{\mathcal{B}} d^3\boldsymbol{q} \int_{\mathcal{B}} d^3\boldsymbol{k} \int_{\mathcal{B}} d^3\boldsymbol{k}'\, \frac{1}{[E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k})]^2 - \hbar^2\omega_I^2(\boldsymbol{q})}. \\ &\quad \times c_\sigma^+(\boldsymbol{k}+\boldsymbol{q}) c_{\sigma'}^+(\boldsymbol{k}') U_I^+(\boldsymbol{k}',\boldsymbol{q}) U_I(\boldsymbol{k},\boldsymbol{q}) c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q}) c_\sigma(\boldsymbol{k}). \end{aligned} \tag{19.103}$$

Phonons with frequencies which are large compared to the electron energy difference,

$$\hbar\omega_I(\boldsymbol{q}) > |E(\boldsymbol{k}+\boldsymbol{q}) - E(\boldsymbol{k})|\,,$$

lower the energy of a two-electron state, thus implying an energetically favorable correlation between electrons. Effectively, a negative coefficient of $c^+_\sigma(\boldsymbol{k}+\boldsymbol{q})c^+_{\sigma'}(\boldsymbol{k}')c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q})c_\sigma(\boldsymbol{k})$ also amounts to an electron-electron attraction. Compare (19.103) with the simplified expression for free fermion operators,

$$H' = \Lambda \sum_{\sigma,\sigma'} \int d^3\boldsymbol{q} \int d^3\boldsymbol{k} \int d^3\boldsymbol{k}'\, c^+_\sigma(\boldsymbol{k}+\boldsymbol{q})c^+_{\sigma'}(\boldsymbol{k}')c_{\sigma'}(\boldsymbol{k}'+\boldsymbol{q})c_\sigma(\boldsymbol{k}).$$

In $\boldsymbol{x}$ space this becomes

$$H' = (2\pi)^3\Lambda \sum_{\sigma,\sigma'} \int d^3\boldsymbol{x}\, \psi^+_\sigma(\boldsymbol{x})\psi^+_{\sigma'}(\boldsymbol{x})\psi_{\sigma'}(\boldsymbol{x})\psi_\sigma(\boldsymbol{x}),$$

which is an attractive interaction for $\Lambda < 0$ and repulsive otherwise.
The possible instability of Fermi surfaces against phonon-induced energetically favored correlations between electrons, and the ensuing suppression of electron scattering, had been identified in the 1950s as the mechanism for low temperature superconductivity[14]. Please consult [4, 15, 20, 23] for textbook discussions of low temperature superconductivity.

19.8 Problems

19.1 Suppose we are using the Born-Oppenheimer approximation for the hydrogen atom, i.e. we treat the proton as fixed at location $\boldsymbol{X}_p = \boldsymbol{0}$. This would yield the same energy levels and energy eigenfunctions that we had found in the exact solution in Chapter 7, *except* that the reduced mass $\mu = m_e m_p/(m_e+m_p)$ would be replaced by the electron mass m_e in the result for the Bohr radius a, and therefore also in the energy eigenvalues and the wave functions.
Show that the corresponding change in the mass value $\delta\mu = m_e - \mu$ satisfies $\delta\mu/\mu = m_e/m_p$. Show also that in the center of mass frame, the neglected kinetic energy of the proton is related to the kinetic energies of the electron and of the relative motion according to

$$K_p = \frac{m_e}{m_p}K_e = \frac{m_e}{m_e+m_p}K_r.$$

Expand the ground state wave function in the Born-Oppenheimer approximation in first order in m_e/m_p in terms of the exact energy eigenstates from Chapter 7.

19.2 Show that the hermitian symmetric matrix $\underline{\tilde{\Omega}^2}(\boldsymbol{k})$ (19.80) with eigenvalues $\omega_I^2(\boldsymbol{k}) \geq 0$ and corresponding normalized eigenvectors $\hat{\boldsymbol{Q}}_I(\boldsymbol{k})$ has square roots $\underline{\tilde{\Omega}}(\boldsymbol{k})$,

$$\underline{\tilde{\Omega}^2}(\boldsymbol{k}) = \underline{\tilde{\Omega}}^2(\boldsymbol{k}).$$

[14] J. Bardeen, L.N. Cooper & J.R. Schrieffer, Phys. Rev. 108, 1175 (1957); see also H. Fröhlich, Phys. Rev. 79, 845 (1950) and J. Bardeen & D. Pines, Phys. Rev. 99, 1140 (1955).

Hint: The column vectors $\hat{\boldsymbol{Q}}_I(\boldsymbol{k})$ can be used to form a unitary matrix $\underline{Q}(\boldsymbol{k})$. The matrix $\underline{Q}(\boldsymbol{k})$ transforms $\underline{\tilde{\Omega}^2}(\boldsymbol{k})$ into diagonal form, or in turn can be used to generate $\underline{\tilde{\Omega}^2}(\boldsymbol{k})$ from its diagonal form $\mathrm{diag}(\omega_1^2(\boldsymbol{k}), \ldots, \omega_{3N}^2(\boldsymbol{k}))$. Use this observation to construct all the possible square roots $\underline{\tilde{\Omega}}(\boldsymbol{k})$ in terms of $\underline{Q}(\boldsymbol{k})$ and $\mathrm{diag}(\pm\omega_1(\boldsymbol{k}), \ldots, \pm\omega_{3N}(\boldsymbol{k}))$.

19.3 Suppose the three particles with masses m and M in Figure 19.8 can only move in one dimension.

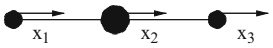


Figure 19.8: Three particles with masses m and M. It is supposed that the particles can only move along the line connecting them.

The potential energy of the system is

$$V = \frac{K}{2}(x_1 - x_2)^2 + \frac{K}{2}(x_2 - x_3)^2.$$

Calculate the eigenvibrations and the eigenfrequencies of the system.

Solution

The potential in matrix notation is

$$V = \frac{K}{2}(x_1, x_2, x_3) \begin{pmatrix} 1 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix},$$

and we have to find the eigenvectors of the corresponding matrix

$$\underline{\Omega^2} = K \begin{pmatrix} \frac{1}{m} & -\frac{1}{\sqrt{mM}} & 0 \\ -\frac{1}{\sqrt{mM}} & \frac{2}{M} & -\frac{1}{\sqrt{mM}} \\ 0 & -\frac{1}{\sqrt{mM}} & \frac{1}{m} \end{pmatrix}, \tag{19.104}$$

cf. 19.62.
Rather than trying to solve

$$\det(\underline{\Omega^2} - \omega^2 \underline{\mathbf{1}}) = 0,$$

we can infer two eigenmodes from the translation and reflection symmetry of the system.
Invariance of the potential under translations $x_1 = x_2 = x_3$ implies that one eigenvector of $\underline{\Omega^2}$ has the form

$$\hat{\boldsymbol{Q}}_{\omega_1=0} = \frac{1}{\sqrt{2m + M}} \begin{pmatrix} \sqrt{m} \\ \sqrt{M} \\ \sqrt{m} \end{pmatrix}.$$

Reflection symmetry also suggests an eigenmode $x_1 = -x_3$, $x_2 = 0$,

$$\hat{\boldsymbol{Q}}_{\omega_2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix},$$

and application of $\underline{\Omega^2}$ yields the corresponding eigenvalue

$$\omega_2^2 = \frac{K}{m}.$$

The remaining eigenvector follows from orthogonality on $\hat{\boldsymbol{Q}}_{\omega_1}$ and $\hat{\boldsymbol{Q}}_{\omega_2}$,

$$\hat{\boldsymbol{Q}}_{\omega_3} = \frac{1}{\sqrt{2(2m+M)}} \begin{pmatrix} \sqrt{M} \\ -2\sqrt{m} \\ \sqrt{M} \end{pmatrix},$$

and application of $\underline{\Omega^2}$ confirms that this is an eigenmode with frequency

$$\omega_3^2 = \frac{K}{m} + \frac{2K}{M}.$$

The eigenmodes are displayed in Figure 19.9.

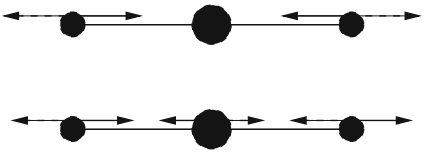


Figure 19.9: The eigenvibrations $\boldsymbol{a}_{\omega_2}$ and $\boldsymbol{a}_{\omega_3}$.

For the actual eigenvibration we have to go back to the amplitude vector $\boldsymbol{a}_{\omega_2}$ (19.60), because different masses participate in the oscillation. The normalized amplitude vector (19.65) is

$$\hat{\boldsymbol{a}}_{\omega_3} = \frac{1}{\sqrt{2mM(2m+M)}} \begin{pmatrix} M \\ -2m \\ M \end{pmatrix}.$$

19.4 Calculate the positive semi-definite square root of the matrix $\underline{\Omega^2}$ in equation (19.104). Use the hint from Problem 2.
Answer:

$$\underline{\Omega} = \frac{\sqrt{K}}{2\sqrt{mM(2m+M)}} \times \begin{pmatrix} M + \sqrt{M(2m+M)} & -2\sqrt{mM} & M - \sqrt{M(2m+M)} \\ -2\sqrt{mM} & 4m & -2\sqrt{mM} \\ M - \sqrt{M(2m+M)} & -2\sqrt{mM} & M + \sqrt{M(2m+M)} \end{pmatrix}.$$

19.5 The electron-phonon interaction Hamiltonian (19.99) is very similar to the electron-photon interaction Hamiltonian in the representation (18.54),

$$H_{e-\gamma} = \frac{e\hbar c}{m_e}\sqrt{\frac{\hbar\mu_0}{(2\pi)^3}}\sum_{\sigma,\alpha}\int\frac{d^3\boldsymbol{q}}{\sqrt{2\omega(\boldsymbol{q})}}\int d^3\boldsymbol{k}\,\boldsymbol{k}\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{q}) \\ \times\left[c_\sigma^+(\boldsymbol{k}+\boldsymbol{q})a_\alpha(\boldsymbol{q})c_\sigma(\boldsymbol{k}) + c_\sigma^+(\boldsymbol{k})a_\alpha^+(\boldsymbol{q})c_\sigma(\boldsymbol{k}+\boldsymbol{q})\right]. \tag{19.105}$$

Which effective electron-electron interaction Hamiltonian $H_{e-e}^{(\gamma)}$ would you get if you eliminate the photon operators through a unitary transformation $|\Phi\rangle \to |\Phi'\rangle = \exp(A)|\Phi\rangle$ similar to the transformation that we performed to transform H_{e-q} into $H_{e-e}^{(q)}$ (19.103)?

Chapter 20

Dimensional Effects in Low-dimensional Systems

Surfaces, interfaces, thin films, and quantum wires provide abundant examples of quasi two-dimensional or one-dimensional systems in science and technology. Quantum mechanics in low dimensions has become an important tool for modeling properties of these systems. Here we wish to go beyond the simple low-dimensional potential models of Chapter 3 and discuss in particular implications of the dependence of energy-dependent Green's functions on the number d of spatial dimensions. However, if it is true that the behavior of electrons in certain systems and parameter ranges can be described by low-dimensional quantum mechanics, then there must also exist ranges of parameters for quasi low-dimensional systems where the behavior of electrons exhibits *inter-dimensional* behavior in the sense that there must exist continuous interpolations e.g. between two-dimensional and three-dimensional behavior. We will see that inter-dimensional (or "dimensionally hybrid") Green's functions provide a possible avenue to the identification and discussion of inter-dimensional behavior in physical systems.

20.1 Quantum mechanics in d dimensions

Suppose an electron is strictly confined to a two-dimensional quantum well. Unless the material in the quantum well has special dielectric properties, that electron would still "know" that it exists in three spatial dimensions, because it feels the $1/r$ Coulomb interaction with other charged particles, and this $1/r$ distance law is characteristic for three dimensions. If the electron would not just be confined to two dimensions, but exist in a genuine two-dimensional world, it would experience a logarithmic distance law for the Coulomb potential. The reason for the $1/r$ Coulomb law in three dimensions is that the solution of the equation

$$\Delta G(r) = -\delta(\boldsymbol{x}) \tag{20.1}$$

R. Dick, *Advanced Quantum Mechanics: Materials and Photons*,
Graduate Texts in Physics, DOI 10.1007/978-1-4419-8077-9_20,
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in three dimensions is given by

$$G(r) = \frac{1}{4\pi r},$$

but in general the solution of equation (20.1) depends on the number d of spatial dimensions. Appendix I explains in detail the derivation of the d-dimensional version of $G(r)$ with the result

$$G_d(r) = \begin{cases} (a-r)/2, & d = 1, \\ -(2\pi)^{-1} \ln(r/a), & d = 2, \\ \Gamma\left(\frac{d-2}{2}\right) \left(4\sqrt{\pi}^d r^{d-2}\right)^{-1}, & d \geq 3. \end{cases} \tag{20.2}$$

The most direct application of these results are electrostatic potentials. Equation (20.1) implies that the electrostatic potential of a point charge q in d dimensions is given by

$$\Phi_d(r) = \frac{q}{\epsilon_0} G_d(r). \tag{20.3}$$

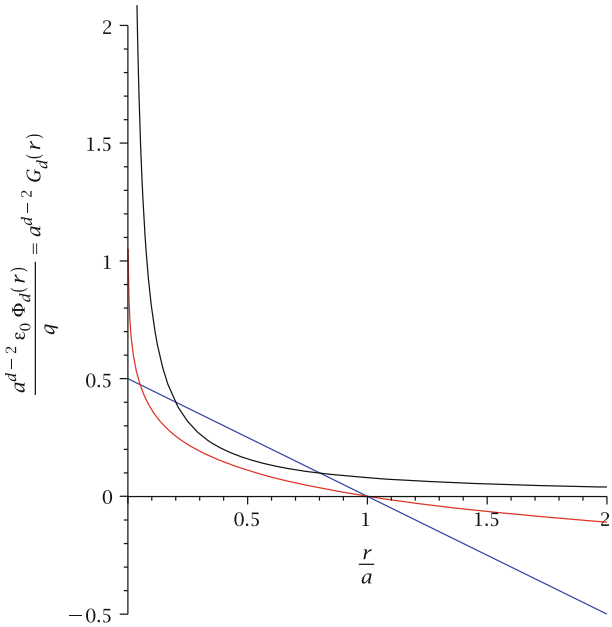


Figure 20.1: The Green's functions (20.2) and the related specific electrostatic potentials $\Phi_d(r)/q$ in 1, 2 and 3 dimensions. The blue curve is for $d = 1$, red is for $d = 2$ and the black curve is the 3-dimensional Coulomb potential.

However, from the point of view of non-relativistic quantum mechanics, the Green's functions (20.2) are the special zero energy values of the energy-dependent free Schrödinger Green's functions, $G_d(r) = G_d(\boldsymbol{x}, E = 0)$. These energy dependent Green's functions statisfy

$$\Delta G_d(\boldsymbol{x}, E) + \frac{2m}{\hbar^2} E G_d(\boldsymbol{x}, E) = -\delta(\boldsymbol{x}). \tag{20.4}$$

We have solved this condition in three dimensions in Section 11.1, see equation (11.12). The solution in d dimensions by two different methods is described in Appendix I, with the result (I.25)

$$\begin{aligned} G_d(\boldsymbol{x}, E) = {} & \frac{\Theta(-E)}{\sqrt{2\pi}^d} \left(\frac{\sqrt{-2mE}}{\hbar r} \right)^{\frac{d-2}{2}} K_{\frac{d-2}{2}} \left(\sqrt{-2mE} \frac{r}{\hbar} \right) \\ & + \mathrm{i} \frac{\pi}{2} \frac{\Theta(E)}{\sqrt{2\pi}^d} \left(\frac{\sqrt{2mE}}{\hbar r} \right)^{\frac{d-2}{2}} H^{(1)}_{\frac{d-2}{2}} \left(\sqrt{2mE} \frac{r}{\hbar} \right). \end{aligned} \tag{20.5}$$

The functions K_ν and $H^{(1)}_\nu$ are modified Bessel functions and Hankel functions of the first kind, respectively, These are exponential functions for $d = 1$ or $d = 3$,

$$K_{-\frac{1}{2}}(x) = K_{\frac{1}{2}}(x) = \sqrt{\frac{\pi}{2x}} \exp(-x), \quad H^{(1)}_{-\frac{1}{2}}(x) = \mathrm{i} H^{(1)}_{\frac{1}{2}}(x) = \sqrt{\frac{2}{\pi x}} \exp(\mathrm{i}x),$$

and therefore

$$\begin{aligned} G_1(x, E) = {} & \frac{\hbar \Theta(-E)}{2\sqrt{-2mE}} \exp\left(-\sqrt{-2mE} \frac{|x|}{\hbar} \right) \\ & + \mathrm{i} \frac{\hbar \Theta(E)}{2\sqrt{2mE}} \exp\left(\mathrm{i}\sqrt{2mE} \frac{|x|}{\hbar} \right), \end{aligned} \tag{20.6}$$

and we recover the already known three-dimensional result from Section 11.1,

$$G_3(\boldsymbol{x}, E) = \frac{\Theta(-E)}{4\pi r} \exp\left(-\sqrt{-2mE} \frac{r}{\hbar} \right) + \frac{\Theta(E)}{4\pi r} \exp\left(\mathrm{i}\sqrt{2mE} \frac{r}{\hbar} \right). \tag{20.7}$$

These results also give us the screened or Yukawa potentials in d dimensions if we substitute $\hbar/\sqrt{-2mE} \to \lambda$, see Figure 20.2.

The figures 20.1 and 20.2 illustrate that long distance effects of interactions become more prominent in lower dimensions, while short distance effects become stronger with increasing number of dimensions.

The Green's function does not only determine interaction potentials, but also has other profound implications for the behavior of particles in d dimensions. We have already seen in Chapter 11 that potential scattering of particles of energy $E = \hbar^2 k^2/2m$ is described by energy-dependent Green's functions.

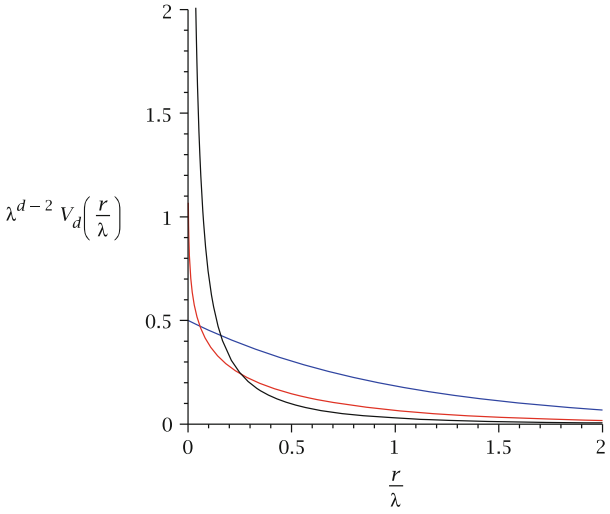


Figure 20.2: Yukawa potentials $V_d(r)$ with screening length λ. The blue curve corresponds to $d = 1$, red to $d = 2$ and black to $d = 3$.

The d-dimensional version of equation (11.14) is

$$\begin{aligned}\psi(\boldsymbol{x}) &= \frac{\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})}{(2\pi)^{d/2}} - \frac{2m}{\hbar^2}\int d^d\boldsymbol{x}'\, G_d(\boldsymbol{x}-\boldsymbol{x}', \hbar^2k^2/2m)V(\boldsymbol{x}')\psi(\boldsymbol{x}') \\ &= \frac{\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})}{(2\pi)^{d/2}} - \frac{\mathrm{i}\pi m}{(2\pi)^{d/2}\hbar^2}\int d^d\boldsymbol{x}' \left(\frac{k}{|\boldsymbol{x}-\boldsymbol{x}'|}\right)^{\frac{d-2}{2}} \\ &\quad \times H^{(1)}_{\frac{d-2}{2}}\left(k|\boldsymbol{x}-\boldsymbol{x}'|\right) V(\boldsymbol{x}')\psi(\boldsymbol{x}'), \end{aligned} \tag{20.8}$$

and we get the d-dimensional version of the leading order Born approximation through the substitution of $\psi(\boldsymbol{x}')$ with the incoming plane wave.

Suppose the scattering potential $V(\boldsymbol{x}')$ is concentrated around $\boldsymbol{x}' = 0$ with finite range R. The asymptotic form of the Hankel function for large argument $x \gg 1$,

$$H^{(1)}_{\frac{d-2}{2}}(x) \to \sqrt{\frac{2}{\pi x}}\exp\left(\mathrm{i}x - \mathrm{i}\pi\frac{d-1}{4}\right),$$

yields the asymptotic form for the scattered wave function in the limit $|\boldsymbol{x}| \gg R$ (here we neglect again the normalization factors $(2\pi)^{-d/2}$ because they cancel

in the cross section),

$$\begin{aligned}\psi(\boldsymbol{x}) &= \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) - \frac{m}{(2\pi)^{(d-1)/2}\hbar^2}\frac{k^{(d-3)/2}}{r^{(d-1)/2}}\exp\left(\mathrm{i}kr - \mathrm{i}\pi\frac{d-3}{4}\right)\\ &\quad\times\int d^d\boldsymbol{x}'\,\exp[\mathrm{i}(\boldsymbol{k}-k\hat{\boldsymbol{x}})\cdot\boldsymbol{x}']V(\boldsymbol{x}')\\ &= \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) + f(k\hat{\boldsymbol{x}}-\boldsymbol{k})\frac{1}{r^{(d-1)/2}}\exp(\mathrm{i}kr)\\ &= \psi^{(\mathrm{in})}(\boldsymbol{x}) + \psi^{(\mathrm{out})}(\boldsymbol{x}),\end{aligned} \tag{20.9}$$

with the scattering amplitude

$$\begin{aligned}f(\Delta\boldsymbol{k}) &= -\frac{mk^{(d-3)/2}}{(2\pi)^{(d-1)/2}\hbar^2}\exp\left(-\mathrm{i}\pi\frac{d-3}{4}\right)\int d^d\boldsymbol{x}\,\exp(-\mathrm{i}\Delta\boldsymbol{k}\cdot\boldsymbol{x})V(\boldsymbol{x})\\ &= -\sqrt{2\pi}\frac{mk^{(d-3)/2}}{\hbar^2}\exp\left(-\mathrm{i}\pi\frac{d-3}{4}\right)V(\Delta\boldsymbol{k}).\end{aligned} \tag{20.10}$$

The d-dimensional version of (11.2),

$$\frac{d\sigma}{d\Omega} = \frac{1}{j_{in}(\hat{\boldsymbol{k}})}\frac{dn(\Omega)}{d\Omega dt} = \lim_{r\to\infty} r^{d-1}\frac{j_{out}(\hat{\boldsymbol{k}}')}{j_{in}(\hat{\boldsymbol{k}})}, \tag{20.11}$$

then yields the same relation between the scattering cross section and the scattering amplitude as in three dimensions,

$$\frac{d\sigma_k}{d\Omega} = |f(k\hat{\boldsymbol{x}}-\boldsymbol{k})|^2\,.$$

Note that the relative prominence of long distance effects in low dimensions should be amplified in scattering effects, because the Green's function generically determines *both* the scattering potentials $V(\boldsymbol{x}')$ *and* the kernels $G_d(\boldsymbol{x}-\boldsymbol{x}', E)$ which are convoluted into the potentials to calculate the scattered wave functions.

Yet another instance where the number of dimensions plays a prominent role is the density of states. We have seen this already in equations (12.11,12.12). However, this result is also closely linked to the energy-dependent Green's functions.

First we note that we can write the generalization of equation (20.4) for the Hamilton operator $H = H_0 + V$,

$$\Delta G_{d,V}(\boldsymbol{x},\boldsymbol{x}';E) + \frac{2m}{\hbar^2}[E - V(\boldsymbol{x})]G_{d,V}(\boldsymbol{x},\boldsymbol{x}';E) = -\delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{20.12}$$

also in representation free operator notation,

$$(E-H)\mathcal{G}_{d,V}(E) = 1, \tag{20.13}$$

where the connection to (20.12) is recovered through the matrix elements[1]

$$\langle \boldsymbol{x}|\mathcal{G}_{d,V}(E)|\boldsymbol{x}'\rangle = -\frac{2m}{\hbar^2} G_{d,V}(\boldsymbol{x},\boldsymbol{x}';E)$$

The solution of (20.13) requires a small complex shift in E to avoid the singularities on the real axis which arise from the real spectrum of H,

$$\mathcal{G}_{d,V}(E) = \frac{1}{E - H + \mathrm{i}\epsilon}.$$

The positive imaginary shift yields the retarded Green's function with only outgoing spherical waves from scattering centers in scattering theory, and only forward evolution in time, see Section 11.1.
The Hamilton operator in the denominator of $\mathcal{G}(E)$ can be replaced by energy eigenvalues if we use energy eigenstates

$$H|E',\nu(E')\rangle = E'|E',\nu(E')\rangle, \quad \sum\!\!\!\!\!\!\int dE'\, d\nu(E')\, |E',\nu(E')\rangle\langle E',\nu(E')| = 1,$$

where $\nu(E')$ is a set of degeneracy indices for energy level E'. This yields

$$\mathcal{G}(E) = \sum\!\!\!\!\!\!\int dE'\, d\nu(E') \frac{|E',\nu(E')\rangle\langle E',\nu(E')|}{E - E' + \mathrm{i}\epsilon}. \tag{20.14}$$

The connection to the density of states follows if we rewrite this with the Sokhotsky-Plemelj relation (2.11),

$$\begin{aligned}\mathcal{G}_{d,V}(E) = {} & \mathcal{P} \sum\!\!\!\!\!\!\int dE'\, d\nu(E') \frac{|E',\nu(E')\rangle\langle E',\nu(E')|}{E - E'} \\ & -\mathrm{i}\pi \sum\!\!\!\!\!\!\int dE'\, d\nu(E')\, \delta(E - E')|E',\nu(E')\rangle\langle E',\nu(E')|. \end{aligned} \tag{20.15}$$

Comparison with equation (12.16) shows that

$$\varrho_d(E,\boldsymbol{x}) = -\frac{1}{\pi}\Im\langle \boldsymbol{x}|\mathcal{G}_{d,V}(E)|\boldsymbol{x}\rangle = \frac{2m}{\pi\hbar^2}\Im\langle \boldsymbol{x}|G_{d,V}(E)|\boldsymbol{x}\rangle. \tag{20.16}$$

In particular, substitution of the free Green's functions (20.5) yields again the result (12.12) which we had initially derived from equation (12.11)

$$\varrho_d(E) = g\Theta(E)\sqrt{\frac{m}{2\pi}}^d \frac{\sqrt{E}^{d-2}}{\Gamma(d/2)\hbar^d}. \tag{20.17}$$

For the derivation of (20.17) from (20.16) and (20.5), we recall that

$$\langle \boldsymbol{x}|G_{d,V}(E)|\boldsymbol{x}'\rangle|_{V=0} \equiv G_{d,V}(\boldsymbol{x},\boldsymbol{x}';E)|_{V=0} = G_d(\boldsymbol{x}-\boldsymbol{x}',E)$$

[1] These concepts are further discussed in Appendix I. However, it is not necessary to read Appendix I before reading this section.

is translation invariant for free particles, and use the property

$$\Re H^{(1)}_{\frac{d-2}{2}}\left(\sqrt{2mE}\frac{r}{\hbar}\right)\Big|_{r\to 0} = J_{\frac{d-2}{2}}\left(\sqrt{2mE}\frac{r}{\hbar}\right)\Big|_{r\to 0} \sim \frac{1}{\Gamma(d/2)}\left(\sqrt{\frac{mE}{2}}\frac{r}{\hbar}\right)^{\frac{d-2}{2}}$$

of the Hankel functions. The spin or helicity factor g arises from the summation over spin states included in the summation over degeneracy indices ν in equation (20.15) if we take into account that the Green's functions (20.5) in the presence of spin multiply $g \times g$ unit matrices in spin space[2].

20.2 Inter-dimensional effects in interfaces and thin layers

The dependence of energy-dependent Green's functions on the number of dimensions begs the question whether this can have observable consequences in (quasi-)two-dimensional or one-dimensional systems like interfaces, layers, thin films, or nanowires. Indeed, the density of states $\varrho_d(E)$ (20.16) is often used to estimate densities of electron states in low-dimensional systems in nanotechnology. However, is this really justified? After all, we are still dealing with electrons with non-vanishing extensions of their wave functions in every direction, including directions perpendicular to any confining potential barriers. Wave functions can be squeezed, but they will will never be genuine two-dimensional or one-dimensional. Furthermore, if the behavior of low-energy particles in confining structures can be approximated by the laws of one-dimensional or two-dimensional quantum mechanics, there must exist a transition regime at higher energy levels, where inter-dimensional effects between low-dimensional and three-dimensional behavior should be observable.

To examine these questions, we consider a model system of elctrons moving in a bulk material which also contains a layer of thickness $2a$ located at $z = z_0$. The potential energy of the electrons inside the layer is shifted by an amount V_0,

$$V(\boldsymbol{x}) \equiv V(z) = V_0\Theta(z_0 + a - z)\Theta(z - z_0 + a), \tag{20.18}$$

and we also assume that electrons in the bulk move with (effective) mass m, while the effective mass inside the layer is m_*. This yields a Hamiltonian which in the first quantized formalism has the form

$$\begin{aligned} H = {} & \frac{\mathbf{p}^2}{2m}\left[1 - \Theta(z_0 + a - z)\Theta(z - z_0 + a)\right] \\ & + \Theta(z_0 + a - z)\Theta(z - z_0 + a)\left(\frac{\mathbf{p}^2}{2m_*} + V_0\right). \end{aligned} \tag{20.19}$$

[2]For spin or helicity, there is actually a transition from a tensor product to a trace operation in making the connection between (20.15) and (20.16): $1 = \sum_s |s\rangle\langle s| \to \sum_s \langle s|s\rangle = g$. Otherwise equation (20.16) would yield the density of states per spin state.

We might expect two-dimensional behavior in the limit $a \to 0$ both from the difference of effective mass in the interface and from the interface potential. Indeed, the different effective mass m_* in the interface implies different propagation properties inside the interface and yields quasi two-dimensional behavior both in terms of propagators and in the the density of states[3], even for vanishing interface potential. In the following we will investigate the emergence of quasi two-dimensional behavior from an attractive interface potential.

Two-dimensional behavior from a thin quantum well

We wish to examine the appearance of quasi two-dimensional behavior from a quantum well potential, i.e. we assume $m_* = m$. An infinitely thin attractive quantum well arises from the potential (20.18) if we set $V_0 = -\mathcal{W}/2a$ and take the limit $a \to 0$,

$$H = \frac{\mathbf{p}^2}{2m} - \mathcal{W}\delta(z - z_0).$$

The corresponding Schrödinger equation separates, and the z component is the Schrödinger equation with the attractive δ potential that we had solved in Section 3.3. This implies three kinds of energy eigenstates. First we have eigenstates which are moving along the interface,

$$\langle \boldsymbol{x}|\boldsymbol{k}_\parallel, \kappa\rangle = \frac{\sqrt{\kappa}}{2\pi} \exp\bigl(\mathrm{i}\boldsymbol{k}_\parallel \cdot \boldsymbol{x}_\parallel - \kappa|z - z_0|\bigr)\,, \quad \kappa = \frac{m}{\hbar^2}\mathcal{W}, \tag{20.20}$$

$$E(\boldsymbol{k}_\parallel, \kappa) = \frac{\hbar^2}{2m}\boldsymbol{k}_\parallel^2 - \frac{m}{2\hbar^2}\mathcal{W}^2.$$

We also have free states with odd or even parity under $z \to 2z_0 - z$, cf. (3.18,3.19),

$$\langle \boldsymbol{x}|\boldsymbol{k}_\parallel, k_\perp, -\rangle = \frac{1}{2\sqrt{\pi^3}} \exp\bigl(\mathrm{i}\boldsymbol{k}_\parallel \cdot \boldsymbol{x}_\parallel\bigr) \sin[k_\perp(z - z_0)], \tag{20.21}$$

$$\langle \boldsymbol{x}|\boldsymbol{k}_\parallel, k_\perp, +\rangle = \exp\bigl(\mathrm{i}\boldsymbol{k}_\parallel \cdot \boldsymbol{x}_\parallel\bigr) \frac{k_\perp \cos[k_\perp(z - z_0)] - \kappa \sin[k_\perp|z - z_0|]}{2\sqrt{\pi^3(\kappa^2 + k_\perp^2)}}. \tag{20.22}$$

The wave number $k_\perp$ in (20.21) and (20.22) is constrained to the positive half-line $k_\perp > 0$, and the energy levels of the free states are

$$E(\boldsymbol{k}_\parallel, k_\perp) = \frac{\hbar^2}{2m}\left(\boldsymbol{k}_\parallel^2 + k_\perp^2\right).$$

The energy-dependent Green's function

$$\langle \boldsymbol{x}_\parallel, z|G(E)|\boldsymbol{x}'_\parallel, z'\rangle \equiv \langle z|G(\boldsymbol{x}_\parallel - \boldsymbol{x}'_\parallel, E)|z'\rangle \equiv -\frac{\hbar^2}{2m}\langle z|\mathcal{G}(\boldsymbol{x}_\parallel - \boldsymbol{x}'_\parallel, E)|z'\rangle$$

[3] R. Dick, Physica E 40, 2973 (2008); Nanoscale Res. Lett. 5, 1546 (2010).

of this system must satisfy

$$\left(\Delta + \frac{2m}{\hbar^2}\left[E + \mathcal{W}\delta(z - z_0)\right]\right)\langle z|G(\boldsymbol{x}_\parallel, E)|z'\rangle = -\delta(\boldsymbol{x}_\parallel)\delta(z - z'). \quad (20.23)$$

We would not have to solve this equation explicitly, since we know the complete set of energy eigenstates of the system. However, there is a neat way to solve these kinds of problems which also works for interfaces in which particles move with different effective mass[4].
We can solve equation (20.23) in a mixed representation using

$$\begin{aligned}\langle \boldsymbol{k}_\parallel, k_\perp|G(E)|\boldsymbol{k}'_\parallel, z'\rangle &= \frac{1}{\sqrt{2\pi}^5}\int d^2\boldsymbol{x}_\parallel \int d^2\boldsymbol{x}'_\parallel \int dz\, \langle \boldsymbol{x}_\parallel, z|G(E)|\boldsymbol{x}'_\parallel, z'\rangle \\ &\quad \times \exp\left[\mathrm{i}\left(\boldsymbol{k}'_\parallel \cdot \boldsymbol{x}'_\parallel - \boldsymbol{k}_\parallel \cdot \boldsymbol{x}_\parallel - k_\perp z\right)\right] \quad (20.24)\\ &= \langle k_\perp|G(\boldsymbol{k}_\parallel, E)|z'\rangle \delta\left(\boldsymbol{k}_\parallel - \boldsymbol{k}'_\parallel\right), \quad (20.25)\end{aligned}$$

$$\begin{aligned}\langle k_\perp|G(\boldsymbol{k}_\parallel, E)|z'\rangle &= \frac{1}{\sqrt{2\pi}}\int d^2\boldsymbol{x}_\parallel \int dz\, \langle z|G(\boldsymbol{x}_\parallel, E)|z'\rangle \\ &\quad \times \exp\left[-\mathrm{i}\left(\boldsymbol{k}_\parallel \cdot \boldsymbol{x}_\parallel + k_\perp z\right)\right]. \quad (20.26)\end{aligned}$$

Substitution into equation (20.23) yields with $\kappa = m\mathcal{W}/\hbar^2$

$$\begin{aligned}\frac{\exp[\mathrm{i}k_\perp(z_0 - z')]}{\sqrt{2\pi}} &= \left(\boldsymbol{k}_\parallel^2 + k_\perp^2 - \frac{2mE}{\hbar^2}\right)\exp(\mathrm{i}k_\perp z_0)\,\langle k_\perp|G(\boldsymbol{k}_\parallel, E)|z'\rangle \\ &\quad -\frac{\kappa}{\pi}\int dq_\perp\, \exp(\mathrm{i}q_\perp z_0)\,\langle q_\perp|G(\boldsymbol{k}_\parallel, E)|z'\rangle. \quad (20.27)\end{aligned}$$

This result implies that the retarded Green's function $\langle k_\perp|G(\boldsymbol{k}_\parallel, E)|z'\rangle$ must have the form

$$\exp(\mathrm{i}k_\perp z_0)\,\langle k_\perp|G(\boldsymbol{k}_\parallel, E)|z'\rangle = \frac{\left(\exp[\mathrm{i}k_\perp(z_0 - z')]/\sqrt{2\pi}\right) + f(\boldsymbol{k}_\parallel, E, z')}{k_\perp^2 + \boldsymbol{k}_\parallel^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon}$$

with the yet to be determined function $f(\boldsymbol{k}_\parallel, E, z')$ satisfying

$$f(\boldsymbol{k}_\parallel, E, z') - \frac{\kappa}{\pi}\int dk_\perp \frac{\left(\exp[\mathrm{i}k_\perp(z_0 - z')]/\sqrt{2\pi}\right) + f(\boldsymbol{k}_\parallel, E, z')}{k_\perp^2 + \boldsymbol{k}_\parallel^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon} = 0.$$

The integral is readily evaluated with the residue theorem,

$$\begin{aligned}\int \frac{dk_\perp}{\pi}\frac{\exp(\mathrm{i}k_\perp z)}{k_\perp^2 + \boldsymbol{k}_\parallel^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon} &= \frac{\Theta(\hbar^2\boldsymbol{k}_\parallel^2 - 2mE)}{\sqrt{\boldsymbol{k}_\parallel^2 - (2mE/\hbar^2)}} \\ \times \exp\left(-\sqrt{\boldsymbol{k}_\parallel^2 - \frac{2mE}{\hbar^2}}|z|\right) &+ \mathrm{i}\frac{\Theta(2mE - \hbar^2\boldsymbol{k}_\parallel^2)}{\sqrt{(2mE/\hbar^2) - \boldsymbol{k}_\parallel^2}}\exp\left(\mathrm{i}\sqrt{\frac{2mE}{\hbar^2} - \boldsymbol{k}_\parallel^2}|z|\right).\end{aligned}$$

[4] R. Dick, Int. J. Theor. Phys. 42, 569 (2003). See also the previous references.

This yields

$$\left[1-\hbar\kappa\left(\frac{\Theta(\hbar^2\boldsymbol{k}_\parallel^2-2mE)}{\sqrt{\hbar^2\boldsymbol{k}_\parallel^2-2mE}}+\mathrm{i}\frac{\Theta(2mE-\hbar^2\boldsymbol{k}_\parallel^2)}{\sqrt{2mE-\hbar^2\boldsymbol{k}_\parallel^2}}\right)\right] f(\boldsymbol{k}_\parallel,E,z')$$
$$=\frac{\hbar\kappa}{\sqrt{2\pi}}\left[\frac{\Theta(\hbar^2\boldsymbol{k}_\parallel^2-2mE)}{\sqrt{\hbar^2\boldsymbol{k}_\parallel^2-2mE}}\exp\left(-\sqrt{\hbar^2\boldsymbol{k}_\parallel^2-2mE}\frac{|z'-z_0|}{\hbar}\right)\right.$$
$$\left.+\mathrm{i}\,\frac{\Theta(2mE-\hbar^2\boldsymbol{k}_\parallel^2)}{\sqrt{2mE-\hbar^2\boldsymbol{k}_\parallel^2}}\exp\left(\mathrm{i}\sqrt{2mE-\hbar^2\boldsymbol{k}_\parallel^2}\frac{|z'-z_0|}{\hbar}\right)\right],$$

and therefore with the proper treatment of poles for retarded Green's functions,

$$\langle k_\perp|G(\boldsymbol{k}_\parallel,E)|z'\rangle=\frac{1}{\sqrt{2\pi}}\frac{1}{k_\perp^2+\boldsymbol{k}_\parallel^2-(2mE/\hbar^2)-\mathrm{i}\epsilon}\left[\exp(-\mathrm{i}k_\perp z')\right.$$
$$+\frac{\hbar\kappa\Theta(\hbar^2\boldsymbol{k}_\parallel^2-2mE)}{\sqrt{\hbar^2\boldsymbol{k}_\parallel^2-2mE}-\hbar\kappa-\mathrm{i}\epsilon}\exp\left(-\mathrm{i}k_\perp z_0-\sqrt{\hbar^2\boldsymbol{k}_\parallel^2-2mE}\frac{|z'-z_0|}{\hbar}\right)$$
$$\left.+\frac{\mathrm{i}\hbar\kappa\Theta(2mE-\hbar^2\boldsymbol{k}_\parallel^2)}{\sqrt{2mE-\hbar^2\boldsymbol{k}_\parallel^2}-\mathrm{i}\hbar\kappa}\exp\left(-\mathrm{i}k_\perp z_0+\mathrm{i}\sqrt{2mE-\hbar^2\boldsymbol{k}_\parallel^2}\frac{|z'-z_0|}{\hbar}\right)\right]. \quad (20.28)$$

Fourier transformation of equation (20.28) with respect to $k_\perp$ yields finally

$$\langle z|G(\boldsymbol{k}_\parallel,E)|z'\rangle=\frac{\hbar\Theta(\hbar^2\boldsymbol{k}_\parallel^2-2mE)}{2\sqrt{\hbar^2\boldsymbol{k}_\parallel^2-2mE}}\left[\exp\left(-\sqrt{\hbar^2\boldsymbol{k}_\parallel^2-2mE}\frac{|z-z'|}{\hbar}\right)\right.$$
$$\left.+\frac{\hbar\kappa}{\sqrt{\hbar^2\boldsymbol{k}_\parallel^2-2mE}-\hbar\kappa-\mathrm{i}\epsilon}\exp\left(-\sqrt{\hbar^2\boldsymbol{k}_\parallel^2-2mE}\frac{|z-z_0|+|z'-z_0|}{\hbar}\right)\right]$$
$$+\mathrm{i}\frac{\hbar\Theta(2mE-\hbar^2\boldsymbol{k}_\parallel^2)}{2\sqrt{2mE-\hbar^2\boldsymbol{k}_\parallel^2}}\left[\exp\left(\mathrm{i}\sqrt{2mE-\hbar^2\boldsymbol{k}_\parallel^2}\frac{|z-z'|}{\hbar}\right)\right.$$
$$\left.+\frac{\mathrm{i}\hbar\kappa}{\sqrt{2mE-\hbar^2\boldsymbol{k}_\parallel^2}-\mathrm{i}\hbar\kappa}\exp\left(\mathrm{i}\sqrt{2mE-\hbar^2\boldsymbol{k}_\parallel^2}\frac{|z-z_0|+|z'-z_0|}{\hbar}\right)\right]. \quad (20.29)$$

The limit $\kappa\to 0$ in equations (20.28,20.29), as well as in equation (20.32) below reproduces the corresponding representations of the free retarded Green's function in three dimensions.

Our results describe the Green's function for a particle in the presence of the thin quantum well, but for arbitrary energy and both near and far from the quantum well. Therefore we cannot easily identify any two-dimensional limit from the Green's function. To explore this question further, we will look at the density of electron states in the presence of the quantum well.

The quantum well at z_0 breaks translational invariance in z direction, and we have with equation (20.16)

$$\varrho(E,z) = \frac{4m}{\pi\hbar^2}\Im\langle \boldsymbol{x}_\parallel, z|G(E)|\boldsymbol{x}_\parallel, z\rangle = \frac{m}{\pi^3\hbar^2}\Im\int d^2\boldsymbol{k}_\parallel\,\langle z|G(\boldsymbol{k}_\parallel, E)|z\rangle,$$

where a factor $g = 2$ was taken into account for spin 1/2 states.
If there is any quasi two-dimensional behavior in this system, we would expect it in the quantum well region. Therefore we use the result (20.29) to calculate the density of states $\varrho(E, z_0)$ in the quantum well. Substitution yields

$$\begin{aligned}\varrho(E,z_0) &= \frac{m}{\pi^3\hbar^2}\Im\int d^2\boldsymbol{k}_\parallel\,\langle z_0|G(\boldsymbol{k}_\parallel, E)|z_0\rangle \\ &= \frac{m}{\pi\hbar}\int_0^\infty dk\,k\,\delta\Big(\sqrt{\hbar^2k^2 - 2mE} - \hbar\kappa\Big) \\ &\quad + \frac{m}{\pi^2\hbar}\Theta(E)\int_0^{\sqrt{2mE}/\hbar} dk\,\frac{k\sqrt{2mE - \hbar^2k^2}}{2mE - \hbar^2k^2 + \hbar^2\kappa^2},\end{aligned}$$

and after evaluation of the integrals,

$$\begin{aligned}\varrho(E,z_0) &= \Theta(2mE + \hbar^2\kappa^2)\kappa\frac{m}{\pi\hbar^2} \\ &\quad + \Theta(E)\frac{m}{\pi^2\hbar^3}\left[\sqrt{2mE} - \hbar\kappa\arctan\left(\frac{\sqrt{2mE}}{\hbar\kappa}\right)\right].\end{aligned} \tag{20.30}$$

We can also express this in terms of the free two-dimensional and three-dimensional densities of electron states (cf. (20.17)),

$$\begin{aligned}\varrho(E,z_0) &= \kappa\varrho_{d=2}\big(E + (\hbar^2\kappa^2/2m)\big) \\ &\quad + \varrho_{d=3}(E)\left[1 - \frac{\hbar\kappa}{\sqrt{2mE}}\arctan\left(\frac{\sqrt{2mE}}{\hbar\kappa}\right)\right].\end{aligned} \tag{20.31}$$

We note that the states which are exponentially suppressed perpendicular to the quantum well indeed contribute a term proportional to the two-dimensional density of states $\varrho_{d=2}(E')$ with the kinetic energy E' of motion of particles along the quantum well, but with a dimensional proportionality constant κ which is the inverse penetration depth of those states. Such a dimensional factor has to be there, because densities of states in three dimensions enumerate states per energy and per volume, while $\varrho_{d=2}(E')$ counts states per energy and per area. Furthermore, the unbound states yield a contribution which approaches the free three-dimensional density of states $\varrho_{d=3}(E)$ in the limit $\kappa \to 0$. The result can also be derived directly from the energy eigenstates (20.20-20.22) and the definition (12.14) of the local density of states, see Problem 7. However, the derivation from the Green's function, while more lengthy for the pure quantum well, has the advantage to also work in the case of an interface in which the electrons move with different effective mass.
The density of states in the quantum well region is displayed for binding energy $B = \hbar^2\kappa^2/2m = 1\,\mathrm{eV}$, mass $m = m_e = 511\,\mathrm{keV}/c^2$, and different energy ranges in Figures 20.3 and 20.4.

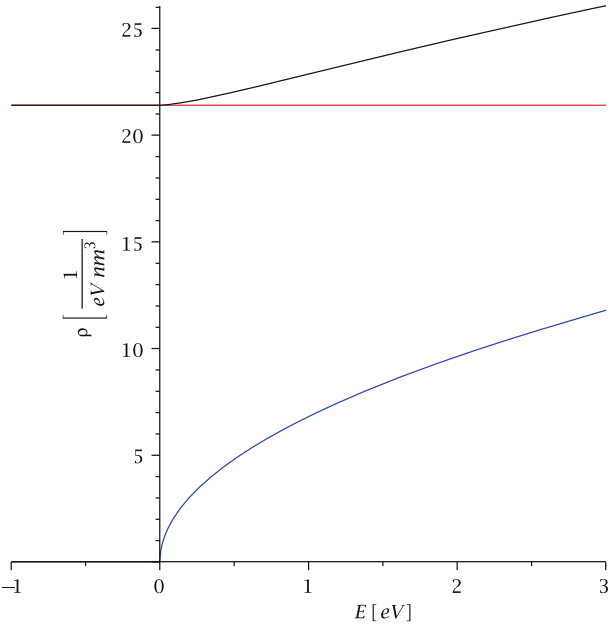


Figure 20.3: The density of states in the quantum well location $z = z_0$ for binding energy $B = 1\,\mathrm{eV}$, mass $m = m_e = 511\,\mathrm{keV}/c^2$, and energies $-B \leq E \leq 3\,\mathrm{eV}$. The red curve is the contribution from states bound inside the quantum well, the blue curve is the pure three-dimensional density of states in absence of a quantum well, and the black curve is the density of states according to equation (20.30).

20.3 Problems

20.1 Derive the d-dimensional version of equation (11.21) for scattering off spherically symmetric potentials.

20.2 Calculate the differential scattering cross sections for the potentials
2a. $V(r) = V_0\Theta(R - r)$,
2b. $V(r) = V_0 \exp(-r/R)$,
2c. $V(r) = V_0 \exp(-r^2/R^2)$,
in d dimensions in Born approximation. What results do you find in particular for $d = 2$?

20.3 Derive the optical theorem in d dimensions.

20.4 The solution (3.16) can also be considered as the bound state in a one-dimensional pointlike quantum dot $V(x) = -\mathcal{W}\delta(x)$,

$$\psi_{d=1}(x) = \kappa \exp(-\kappa|x|), \quad \kappa = \frac{m}{\hbar^2}\mathcal{W},$$

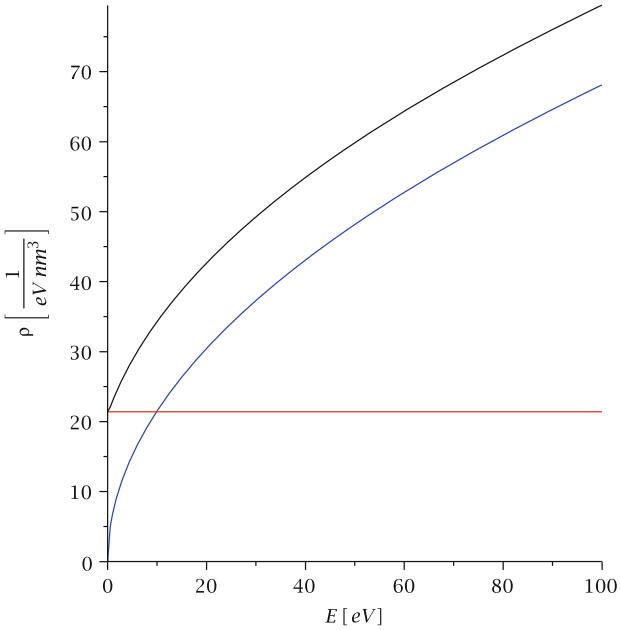


Figure 20.4: The density of states (20.30) in the quantum well location $z = z_0$ for higher energies $0 \leq E \leq 100\,\text{eV}$. The binding energy, mass and color coding are the same as in Figure 20.3. The full density of states (20.30) approximates the three-dimensional $\sqrt{E}$ behavior for energies $E \gg B$, but there remains a finite offset compared to $\varrho_{d=3}$ due to the presence of the quantum well.

with binding energy

$$B = -E = \frac{\hbar^2\kappa^2}{2m} = \frac{m}{2\hbar^2}\mathcal{W}^2.$$

No such states exist for higher-dimensional pointlike quantum dots $V(\boldsymbol{x}) = -\mathcal{W}\delta(\boldsymbol{x})$, unless we also let the depth $\mathcal{W}$ go to zero in a judicious way.
Show that the following wave functions describe bound states in two-dimensional and three-dimensional pointlike quantum dots if we let $\mathcal{W}$ go to zero,

$$\psi_{d=2}(r) = \frac{\kappa}{\sqrt{\pi}}K_0(\kappa r), \quad \psi_{d=3}(r) = \sqrt{\frac{\kappa}{2\pi}}\frac{\exp(-\kappa r)}{r}.$$

The binding energy of the states is

$$B = -E = \frac{\hbar^2\kappa^2}{2m}.$$

Hint: Show that the bound states must be proportional to the energy-dependent retarded Green's functions.

Note that we cannot extend this construction to four or more dimensions because the corresponding Green's functions are not square integrable any more.

20.5 Suppose we consider a proton and an electron in $d \geq 3$ spatial dimensions. The electromagnetic interaction potential of these particles is

$$V_d(r) = -\frac{e^2}{\epsilon_0} G_d(r).$$

Suppose that there are normalizable bound energy eigenstates in this system. Which relation between the expectation values $\langle K \rangle$ and $\langle V \rangle$ of kinetic and potential energy would then be implied by the virial theorem?
Can atoms exist in $d \geq 4$ dimensions?

20.6 Show that substitution of the Fourier transform

$$\begin{aligned}\langle \boldsymbol{k}_\parallel, k_\perp | G(E) | \boldsymbol{k}'_\parallel, k'_\perp \rangle &= \int d^2\boldsymbol{x}_\parallel \int d^2\boldsymbol{x}'_\parallel \int dz \int dz' \, \frac{\langle \boldsymbol{x}_\parallel, z | G(E) | \boldsymbol{x}'_\parallel, z' \rangle}{(2\pi)^3} \\ &\quad \times \exp\left[\mathrm{i}\left(\boldsymbol{k}'_\parallel \cdot \boldsymbol{x}'_\parallel + k'_\perp z' - \boldsymbol{k}_\parallel \cdot \boldsymbol{x}_\parallel - k_\perp z\right)\right] \\ &= \langle k_\perp | G(\boldsymbol{k}_\parallel, E) | k'_\perp \rangle \delta\left(\boldsymbol{k}_\parallel - \boldsymbol{k}'_\parallel\right),\end{aligned}$$

$$\begin{aligned}\langle k_\perp | G(\boldsymbol{k}_\parallel, E) | k'_\perp \rangle &= \frac{1}{2\pi} \int d^2\boldsymbol{x}_\parallel \int dz \, \langle z | G(\boldsymbol{x}_\parallel, E) | z' \rangle \\ &\quad \times \exp\left[-\mathrm{i}\left(\boldsymbol{k}_\parallel \cdot \boldsymbol{x}_\parallel + k_\perp z - k'_\perp z'\right)\right]\end{aligned}$$

in equation (20.23) yields with the same technique that we used to solve (20.27) the result

$$\begin{aligned}\langle k_\perp | G(E, \boldsymbol{k}_\parallel) | k'_\perp \rangle &= \frac{1}{k_\perp^2 + \boldsymbol{k}_\parallel^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon} \Bigg[\delta(k_\perp - k'_\perp) \\ &+ \frac{\kappa}{\pi} \frac{\exp[\mathrm{i}(k'_\perp - k_\perp) z_0]}{k'^2_\perp + \boldsymbol{k}_\parallel^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon} \left(\frac{\sqrt{\hbar^2 \boldsymbol{k}_\parallel^2 - 2mE}\, \Theta(\hbar^2 \boldsymbol{k}_\parallel^2 - 2mE)}{\sqrt{\hbar^2 \boldsymbol{k}_\parallel^2 - 2mE} - \hbar\kappa - \mathrm{i}\epsilon} \right. \\ &+ \left. \frac{\sqrt{2mE - \hbar^2 \boldsymbol{k}_\parallel^2}\, \Theta(2mE - \hbar^2 \boldsymbol{k}_\parallel^2)}{\sqrt{2mE - \hbar^2 \boldsymbol{k}_\parallel^2} - \mathrm{i}\hbar\kappa} \right) \Bigg].\end{aligned} \tag{20.32}$$

Show also that Fourier transformation yields again the result (20.28).

20.7 Derive the result (20.30) directly from the energy eigenstates (20.20), (20.21) and (20.22) for particles in the presence of the quantum well.

Solution

The decomposition of unity in terms of the eigenstates is

$$\int d^2\boldsymbol{k}_\parallel \, |\boldsymbol{k}_\parallel, \kappa\rangle\langle \boldsymbol{k}_\parallel, \kappa| + \sum_{\pm} \int d^2\boldsymbol{k}_\parallel \int_0^\infty dk_\perp \, |\boldsymbol{k}_\parallel, k_\perp, \pm\rangle\langle \boldsymbol{k}_\parallel, k_\perp, \pm| = 1.$$

For the application of the definition (12.14) we have to take into account that

$$d^2\boldsymbol{k}_\parallel = k_\parallel dk_\parallel d\varphi \to \frac{m}{\hbar^2} dE d\varphi$$

holds both for the two dimensional integration measure $d^2\boldsymbol{k}_\parallel$ from $E = \hbar^2(\boldsymbol{k}_\parallel^2 - \kappa^2)/2m$, and also in the three-dimensional integration measure $d^2\boldsymbol{k}_\parallel \wedge dk_\perp$, where $E = \hbar^2(\boldsymbol{k}_\parallel^2 + k_\perp^2)/2m$. This yields with a factor of 4π from $g = 2$ for electrons and from integration over φ the result

$$\varrho(E, z_0) = \frac{4\pi m}{\hbar^2} \left(\Theta(2mE + \hbar^2\kappa^2) \frac{\kappa}{4\pi^2} + \Theta(E) \int_0^{\sqrt{2mE}/\hbar} \frac{k_\perp^2 dk_\perp}{4\pi^3(\kappa^2 + k_\perp^2)} \right).$$

Evaluation of the integral yields again the result (20.30).

Chapter 21

Klein-Gordon and Dirac Fields

The quantized Maxwell field provided us already with an example of a relativistic quantum field theory. The description of relativistic charged particles, on the other hand, requires Klein-Gordon fields for scalar particles and Dirac fields for fermions. Relativistic fields are apparently relevant for high energy physics. However, relativistic effects are also important in photon-matter interactions and spectroscopy, and for the generation of high energy photons from ultra-relativistic electrons in synchrotrons. Quasi-relativistic effects from linear dispersion relations $E \propto \boldsymbol{p}$ in Graphene have also reinvigorated the need to reconsider the role of Dirac and Weyl equations in materials science. We start our discussion of relativistic matter fields with the simpler Klein-Gordon equation and then move on to the more widely applicable Dirac equation.

21.1 The Klein-Gordon equation

A limitation of the Schrödinger equation in the framework of ordinary quantum mechanics is its lack of covariance under Lorentz transformations[1]. On the other hand, we have encountered an example of a relativistic wave equation in Chapter 18, viz. the inhomogeneous Maxwell equation

$$\partial_\mu \left(\partial^\mu A^\nu - \partial^\nu A^\mu\right) = -\mu_0 j^\nu.$$

This equation is manifestly covariant (or rather, form invariant) under Lorentz transformations because it is composed of quantities with simple tensorial transformation behavior under Lorentz transformations, and it relates a 4-vector $\partial_\mu F^{\mu\nu}$ to a 4-vector j^ν, such that the equation holds in this form in every inertial reference frame.
Another, simple reasoning to come up with a relativistic wave equation goes as follows. We know that the standard Schrödinger equation for a free massive

[1]However, we will see that in the second quantized formalism in the Heisenberg and Dirac pictures, the time evolution of the field operators is given by Heisenberg equations of motion, and the corresponding time evolution of states in the Schrödinger and Dirac pictures is given by corresponding Schrödinger equations with relativistic Hamiltonians.

R. Dick, *Advanced Quantum Mechanics: Materials and Photons*,
Graduate Texts in Physics, DOI 10.1007/978-1-4419-8077-9_21,
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particle arises from the non-relativistic energy-momentum dispersion relation $E = -cp_0 = \boldsymbol{p}^2/2m$ upon substitution of the classical energy-momentum vector through differential operators, $p_\mu \to -\mathrm{i}\hbar\partial_\mu$. Following the same procedure in the relativistic dispersion relation

$$-\frac{E^2}{c^2} + \boldsymbol{p}^2 + m^2c^2 = p^2 + m^2c^2 = 0$$

yields the free Klein-Gordon equation[2]

$$\left(\partial^2 - \frac{m^2c^2}{\hbar^2}\right)\phi(x) = \left(\Delta - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\right)\phi(x) = 0. \tag{21.1}$$

Furthermore, the gauge principle or minimal coupling prescription $\partial_\mu \to D_\mu = \partial_\mu - \mathrm{i}(q/\hbar)A_\mu$ yields the coupling of the charged Klein-Gordon field to electromagnetic potentials,

$$\left[\left(\partial - \mathrm{i}\frac{q}{\hbar}A(x)\right)^2 - \frac{m^2c^2}{\hbar^2}\right]\phi(x) = \left[\left(\boldsymbol{\nabla} - \mathrm{i}\frac{q}{\hbar}\boldsymbol{A}(x)\right)^2 - \frac{1}{c^2}\left(\frac{\partial}{\partial t} + \mathrm{i}\frac{q}{\hbar}\Phi(x)\right)^2 - \frac{m^2c^2}{\hbar^2}\right]\phi(x) = 0. \tag{21.2}$$

The Klein-Gordon field is relevant in particle physics. E.g. π-mesons are described by Klein-Gordon fields as soon as their kinetic energy becomes comparable to their mass $mc^2 \simeq 140\,\mathrm{MeV}$, when relativistic effects have to be taken into account. Another important application of the Klein-Gordon field is the Higgs field for electroweak symmetry breaking in the Standard Model of particle physics.
The Klein-Gordon field also provides a simple introduction into the relativistic quantum mechanics of charged particles, and therefore is also useful as a preparation for the study of the Dirac field.

Mode expansion and quantization of the Klein-Gordon field

Fourier transformation of equation (21.1) yields the general solution of the free Klein-Gordon equation,

$$\phi(\boldsymbol{x},t) = \frac{1}{\sqrt{2\pi}^3}\int \frac{d^3\boldsymbol{k}}{\sqrt{2\omega_{\boldsymbol{k}}}}\Big(a(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - \omega_{\boldsymbol{k}}t)] + b^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x} - \omega_{\boldsymbol{k}}t)]\Big) \tag{21.3}$$

with

$$\omega_{\boldsymbol{k}} = c\sqrt{\boldsymbol{k}^2 + \frac{m^2c^2}{\hbar^2}}.$$

[2] E. Schrödinger, Annalen Phys. 386, 109 (1926); W. Gordon, Z. Phys. 40, 117 (1926); O. Klein, Z. Phys. 41, 407 (1927).

For the inversion of the Fourier transformation we need equation (21.3) and

$$\dot\phi(\boldsymbol{x},t) = \frac{\mathrm{i}}{\sqrt{2\pi}^3}\int d^3\boldsymbol{k}\,\sqrt{\frac{\omega_{\boldsymbol{k}}}{2}}\Big(-a(\boldsymbol{k})\exp[\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_{\boldsymbol{k}}t)] + b^+(\boldsymbol{k})\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_{\boldsymbol{k}}t)]\Big).$$

Inversion of both equations yields

$$\begin{aligned} a(\boldsymbol{k}) &= \frac{1}{\sqrt{2\pi}^3}\int\frac{d^3\boldsymbol{x}}{\sqrt{2\omega_{\boldsymbol{k}}}}\Big(\omega_{\boldsymbol{k}}\phi(\boldsymbol{x},t)+\mathrm{i}\dot\phi(\boldsymbol{x},t)\Big)\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_{\boldsymbol{k}}t)] \\ &= \frac{1}{\sqrt{2\pi}^3}\int\frac{d^3\boldsymbol{x}}{\sqrt{2\omega_{\boldsymbol{k}}}}\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_{\boldsymbol{k}}t)]\,\mathrm{i}\overset{\leftrightarrow}{\partial_t}\,\phi(\boldsymbol{x},t), \qquad (21.4) \\ b(\boldsymbol{k}) &= \frac{1}{\sqrt{2\pi}^3}\int\frac{d^3\boldsymbol{x}}{\sqrt{2\omega_{\boldsymbol{k}}}}\Big(\omega_{\boldsymbol{k}}\phi^+(\boldsymbol{x},t)+\mathrm{i}\dot\phi^+(\boldsymbol{x},t)\Big)\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_{\boldsymbol{k}}t)] \\ &= \frac{1}{\sqrt{2\pi}^3}\int\frac{d^3\boldsymbol{x}}{\sqrt{2\omega_{\boldsymbol{k}}}}\exp[-\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{x}-\omega_{\boldsymbol{k}}t)]\,\mathrm{i}\overset{\leftrightarrow}{\partial_t}\,\phi^+(\boldsymbol{x},t). \qquad (21.5) \end{aligned}$$

Here the alternating derivative is defined as

$$f\overset{\leftrightarrow}{\partial_t}\,g = f\frac{\partial g}{\partial t}-\frac{\partial f}{\partial t}g.$$

Substituting (21.4,21.5) back into (21.3) and formal exchange of integrations yields

$$\phi(\boldsymbol{x},t) = \int d^3\boldsymbol{x}'\,\mathcal{K}(\boldsymbol{x}-\boldsymbol{x}',t-t')\overset{\leftrightarrow}{\partial_{t'}}\,\phi(\boldsymbol{x}',t')$$

with the time evolution kernel for free scalar fields,

$$\mathcal{K}(\boldsymbol{x},t) = \frac{1}{(2\pi)^3}\int\frac{d^3\boldsymbol{k}}{\omega_{\boldsymbol{k}}}\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})\sin(\omega_{\boldsymbol{k}}t). \qquad (21.6)$$

This distribution satisfies the initial value problem

$$\left(\partial^2-\frac{m^2c^2}{\hbar^2}\right)\mathcal{K}(\boldsymbol{x},t)=0,\quad \mathcal{K}(\boldsymbol{x},0)=0,\quad \frac{\partial}{\partial t}\mathcal{K}(\boldsymbol{x},t)\Big|_{t=0}=\delta(\boldsymbol{x}).$$

For canonical quantization we need the Lagrange density for the complex Klein-Gordon field

$$\begin{aligned} \mathcal{L} &= \hbar\dot\phi^+\cdot\dot\phi-\hbar c^2\boldsymbol{\nabla}\phi^+\cdot\boldsymbol{\nabla}\phi-\frac{m^2c^4}{\hbar}\phi^+\cdot\phi \\ &= -\hbar c^2\partial\phi^+\cdot\partial\phi-\frac{m^2c^4}{\hbar}\phi^+\cdot\phi, \qquad (21.7) \end{aligned}$$

or the real Klein-Gordon field

$$\mathcal{L} = \frac{\hbar}{2}\dot\phi\cdot\dot\phi-\frac{\hbar c^2}{2}\boldsymbol{\nabla}\phi\cdot\boldsymbol{\nabla}\phi-\frac{m^2c^4}{2\hbar}\phi^2 = -\frac{\hbar c^2}{2}(\partial\phi)^2-\frac{m^2c^4}{2\hbar}\phi^2. \qquad (21.8)$$

In the following we will continue with the discussion of the complex Klein-Gordon field.
Canonical quantization proceeds from (21.7) without any problems. The conjugate momenta

$$\Pi_\phi = \frac{\partial \mathcal{L}}{\partial \dot{\phi}} = \hbar \dot{\phi}^+, \quad \Pi_{\phi^+} = \frac{\partial \mathcal{L}}{\partial \dot{\phi}^+} = \hbar \dot{\phi},$$

yield the canonical commutation relations in $\boldsymbol{x}$ space,

$$[\phi(\boldsymbol{x},t), \dot{\phi}^+(\boldsymbol{x}',t)] = \mathrm{i}\delta(\boldsymbol{x}-\boldsymbol{x}'), \quad [\phi^+(\boldsymbol{x},t), \dot{\phi}(\boldsymbol{x}',t)] = \mathrm{i}\delta(\boldsymbol{x}-\boldsymbol{x}'),$$

$$[\phi(\boldsymbol{x},t), \dot{\phi}(\boldsymbol{x}',t)] = 0, \quad [\phi(\boldsymbol{x},t), \phi(\boldsymbol{x}',t)] = 0, [\phi(\boldsymbol{x},t), \phi^+(\boldsymbol{x}',t)] = 0,$$

$$[\dot{\phi}(\boldsymbol{x},t), \dot{\phi}(\boldsymbol{x}',t)] = 0, \quad [\dot{\phi}(\boldsymbol{x},t), \dot{\phi}^+(\boldsymbol{x}',t)] = 0,$$

and in $\boldsymbol{k}$ space,

$$[a(\boldsymbol{k}), a^+(\boldsymbol{k}')] = \delta(\boldsymbol{k}-\boldsymbol{k}'), \quad [a(\boldsymbol{k}), a(\boldsymbol{k}')] = 0, \quad [b(\boldsymbol{k}), b^+(\boldsymbol{k}')] = \delta(\boldsymbol{k}-\boldsymbol{k}'),$$

$$[b(\boldsymbol{k}), b(\boldsymbol{k}')] = 0, \quad [a(\boldsymbol{k}), b(\boldsymbol{k}')] = 0, \quad [a(\boldsymbol{k}), b^+(\boldsymbol{k}')] = 0.$$

The Lagrangian for interacting Klein-Gordon and Maxwell fields is

$$\mathcal{L} = -\frac{c^2}{\hbar}\left(\hbar\partial_\mu\phi^+ + \mathrm{i}q\phi^+ \cdot A_\mu\right) \cdot (\hbar\partial^\mu\phi - \mathrm{i}qA^\mu \cdot \phi) - \frac{m^2c^4}{\hbar}\phi^+ \cdot \phi - \frac{1}{4\mu_0}F_{\mu\nu}F^{\mu\nu}. \tag{21.9}$$

Charge-current operators of the Klein-Gordon field

The Klein-Gordon Lagrangian (21.7) is invariant under phase transformations

$$\phi(x) \to \phi'(x) = \exp\left(\mathrm{i}\frac{q}{\hbar}\alpha\right)\phi(x), \quad \delta\phi(x) = \mathrm{i}\frac{q}{\hbar}\alpha\phi(x).$$

According to Section 16.2 this implies a local conservation law (16.11) for a conserved charge Q. After cancelling the superfluous factor α, the charge following from (16.12) is (after normal ordering of the integrand in $\boldsymbol{k}$ space)

$$\begin{aligned} Q &= -\mathrm{i}\frac{q}{\hbar}\int d^3\boldsymbol{x}\left(\frac{\partial\mathcal{L}}{\partial\dot{\phi}}\cdot\phi - \phi^+\cdot\frac{\partial\mathcal{L}}{\partial\dot{\phi}^+}\right) \\ &= -\mathrm{i}q\int d^3\boldsymbol{x}\left(\dot{\phi}^+(\boldsymbol{x},t)\cdot\phi(\boldsymbol{x},t) - \phi^+(\boldsymbol{x},t)\cdot\dot{\phi}(\boldsymbol{x},t)\right) \\ &= q\int d^3\boldsymbol{k}\left(a^+(\boldsymbol{k})a(\boldsymbol{k}) - b^+(\boldsymbol{k})b(\boldsymbol{k})\right). \end{aligned} \tag{21.10}$$

The charge density $\mathrm{i}q\phi^+ \overset{\leftrightarrow}{\partial_t} \phi$ is not positive definite, and therefore division of the charge density by q does not yield a probability density for the location of

a particle, contrary to the Schrödinger field. Lack of a single particle interpretation is a generic property of relativistic fields which we had also encountered for the Maxwell field.
Although it is not a commonly used quantity, it is also interesting to see the resulting expression for the current operator,

$$\begin{aligned}\boldsymbol{J} &= \int d^3\boldsymbol{x}\, \boldsymbol{j}(\boldsymbol{x},t) = -\mathrm{i}\frac{q}{\hbar}\int d^3\boldsymbol{x}\left(\frac{\partial\mathcal{L}}{\partial\boldsymbol{\nabla}\phi}\cdot\phi - \phi^+\cdot\frac{\partial\mathcal{L}}{\partial\boldsymbol{\nabla}\phi^+}\right)\\ &= \mathrm{i}qc^2\int d^3\boldsymbol{x}\left(\boldsymbol{\nabla}\phi^+(\boldsymbol{x},t)\cdot\phi(\boldsymbol{x},t) - \phi^+(\boldsymbol{x},t)\cdot\boldsymbol{\nabla}\phi(\boldsymbol{x},t)\right)\\ &= q\int d^3\boldsymbol{k}\frac{c^2\boldsymbol{k}}{\omega_{\boldsymbol{k}}}\left(a^+(\boldsymbol{k})a(\boldsymbol{k}) - b^+(\boldsymbol{k})b(\boldsymbol{k})\right).\end{aligned} \tag{21.11}$$

This result makes sense because the factor

$$\boldsymbol{v} = \frac{\partial\omega_{\boldsymbol{k}}}{\partial\boldsymbol{k}} = \frac{c^2\boldsymbol{k}}{\omega_{\boldsymbol{k}}}$$

is the group velocity of Klein-Gordon wave packets.

Hamiltonian and momentum operators for the Klein-Gordon field

The invariance of the Klein-Gordon Lagrangian (21.7) under constant translations

$$x^\mu \to x'^\mu = x^\mu + \delta x^\mu$$

implies a local conservation law (16.13) with corresponding conserved Hamilton and momentum operators (16.15),

$$\begin{aligned}\mathcal{H} &= -\Theta_0{}^0 = \hbar\dot\phi^+\cdot\dot\phi + \hbar c^2\boldsymbol{\nabla}\phi^+\cdot\boldsymbol{\nabla}\phi + \frac{m^2c^4}{\hbar}\phi^+\cdot\phi,\\ H &= \int d^3\boldsymbol{x}\,\mathcal{H} = \int d^3\boldsymbol{k}\,\hbar\omega_{\boldsymbol{k}}\big(a^+(\boldsymbol{k})a(\boldsymbol{k}) + b^+(\boldsymbol{k})b(\boldsymbol{k})\big),\end{aligned} \tag{21.12}$$

$$\begin{aligned}\boldsymbol{\mathcal{P}} &= \frac{1}{c}\boldsymbol{e}_i\Theta_i{}^0 = -\frac{\partial\mathcal{L}}{\partial\dot\phi}\cdot\boldsymbol{\nabla}\phi - \boldsymbol{\nabla}\phi^+\cdot\frac{\partial\mathcal{L}}{\partial\dot\phi^+} = -\hbar\dot\phi^+\cdot\boldsymbol{\nabla}\phi - \hbar\boldsymbol{\nabla}\phi^+\cdot\dot\phi,\\ \boldsymbol{P} &= \int d^3\boldsymbol{x}\,\boldsymbol{\mathcal{P}} = \int d^3\boldsymbol{k}\,\hbar\boldsymbol{k}\big(a^+(\boldsymbol{k})a(\boldsymbol{k}) + b^+(\boldsymbol{k})b(\boldsymbol{k})\big).\end{aligned} \tag{21.13}$$

The commutation relations and the charge operator (21.10), the current operator (21.11), the Hamilton operator (21.12), and the momentum operators (21.13) imply that the operator $a^+(\boldsymbol{k})$ creates a particle of momentum $\hbar\boldsymbol{k}$, energy $\hbar\omega_{\boldsymbol{k}}$ and charge q, while $b^+(\boldsymbol{k})$ creates a particle of momentum $\hbar\boldsymbol{k}$, energy $\hbar\omega_{\boldsymbol{k}}$ and charge $-q$.

The operators (21.3) and $a(\boldsymbol{k},t) = a(\boldsymbol{k})\exp(-\mathrm{i}\omega_{\boldsymbol{k}}t)$, $a^+(\boldsymbol{k},t) = a^+(\boldsymbol{k})\exp(\mathrm{i}\omega_{\boldsymbol{k}}t)$ are the field operators in the Dirac picture, or the free field operators in the Heisenberg picture. They satisfy the Heisenberg evolution equations

$$\frac{\partial}{\partial t}a(\boldsymbol{k},t) = \frac{\mathrm{i}}{\hbar}[H, a(\boldsymbol{k},t)], \quad \frac{\partial}{\partial t}\phi(\boldsymbol{x},t) = \frac{\mathrm{i}}{\hbar}[H, \phi(\boldsymbol{x},t)],$$

with the free Hamiltonian (21.12). The corresponding integrals follow in the standard way,

$$a(\boldsymbol{k},t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)a(\boldsymbol{k})\exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right),$$

$$\phi(\boldsymbol{x},t) = \exp\left(\frac{\mathrm{i}}{\hbar}Ht\right)\phi(\boldsymbol{x})\exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right),$$

etc. In the Schrödinger picture theory, this amounts to operators $a(\boldsymbol{k})$, $\phi(\boldsymbol{x})$, and time evolution of the states

$$\mathrm{i}\hbar\frac{d}{dt}|\Psi(t)\rangle = H|\Psi(t)\rangle$$

with the free Hamiltonian (21.12) for free states, or a corresponding minimally coupled Hamiltonian which follows from (21.9) for interacting states. This is the statement that we have Heisenberg and Schrödinger type evolution equations also in relativistic quantum field theory.

Non-relativistic limit of the Klein-Gordon field

We have in the non-relativistic limit

$$\omega_{\boldsymbol{k}} = c\sqrt{\boldsymbol{k}^2 + \frac{m^2c^2}{\hbar^2}} \simeq \frac{mc^2}{\hbar} + \frac{\hbar\boldsymbol{k}^2}{2m},$$

i.e. we have to extract the rest mass term $\exp(-\mathrm{i}mc^2t/\hbar)$ from the first exponential factor in equation (21.3) to get the standard time evolution $\psi \sim \exp(-\mathrm{i}\hbar\boldsymbol{k}^2t/2m)$ of a free Schrödinger field. However, then we get an even faster oscillation $\exp(2\mathrm{i}mc^2t/\hbar)$ in the second exponential term. Therefore the amplitude $|\langle b^+(\boldsymbol{k})\rangle|$ of the second term must be small compared to the amplitude $|\langle a(\boldsymbol{k})\rangle|$ of the first term in the non-relativistic limit.
Extraction of the rest mass term means that for $\hbar|\boldsymbol{k}| \ll mc$ and $|\langle b^+(\boldsymbol{k})\rangle| \ll |\langle a(\boldsymbol{k})\rangle|$ we set

$$\phi(\boldsymbol{x},t) \simeq \sqrt{\frac{\hbar}{2mc^2}}\psi(\boldsymbol{x},t)\exp\left(-\mathrm{i}\frac{mc^2}{\hbar}t\right). \tag{21.14}$$

Substitution into the charge, current, energy and momentum densities of the Klein-Gordon field then yields the corresponding expressions for the

Schrödinger field,

$$\begin{aligned}
\varrho &= -\mathrm{i}q\left(\dot{\phi}^+\cdot\phi-\phi^+\cdot\dot{\phi}\right)\simeq q\psi^+\psi,\\
\boldsymbol{j} &= \mathrm{i}qc^2\left(\boldsymbol{\nabla}\phi^+\cdot\phi-\phi^+\cdot\boldsymbol{\nabla}\phi\right)=q\frac{\hbar}{2m\mathrm{i}}\left(\psi^+\cdot\boldsymbol{\nabla}\psi-\psi\cdot\boldsymbol{\nabla}\psi^+\right),\\
\mathcal{H} &= \hbar\dot{\phi}^+\cdot\dot{\phi}+\hbar c^2\boldsymbol{\nabla}\phi^+\cdot\boldsymbol{\nabla}\phi+\frac{m^2c^4}{\hbar}\phi^+\cdot\phi\simeq\frac{\hbar^2}{2m}\boldsymbol{\nabla}\psi^+\cdot\boldsymbol{\nabla}\psi+mc^2\psi^+\cdot\psi,\\
\boldsymbol{\mathcal{P}} &= -\hbar\dot{\phi}^+\cdot\boldsymbol{\nabla}\phi-\hbar\boldsymbol{\nabla}\phi^+\cdot\dot{\phi}\simeq\frac{\hbar}{2\mathrm{i}}\left(\psi^+\cdot\boldsymbol{\nabla}\psi-\psi\cdot\boldsymbol{\nabla}\psi^+\right)=\frac{m}{q}\boldsymbol{j}.
\end{aligned}$$

Furthermore, the free Klein-Gordon equation (21.1) becomes with

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\phi(\boldsymbol{x},t)\simeq\sqrt{\frac{\hbar}{2mc^2}}\exp\left(-\mathrm{i}\frac{mc^2}{\hbar}t\right)\left(-\frac{m^2c^2}{\hbar^2}\psi(\boldsymbol{x},t)-\mathrm{i}\frac{2m}{\hbar}\frac{\partial}{\partial t}\psi(\boldsymbol{x},t)\right)$$

the free Schrödinger equation

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\psi=-\frac{\hbar^2}{2m}\Delta\psi.$$

For the non-relativistic limit of the real Klein-Gordon field we can set

$$\phi(\boldsymbol{x},t)\simeq\sqrt{\frac{\hbar}{2mc^2}}\left(\psi(\boldsymbol{x},t)\exp\left(-\mathrm{i}\frac{mc^2}{\hbar}t\right)+\psi^+(\boldsymbol{x},t)\exp\left(\mathrm{i}\frac{mc^2}{\hbar}t\right)\right),$$

but we have to include first order time derivatives of $\psi(\boldsymbol{x},t)$ and $\psi^+(\boldsymbol{x},t)$ in the evaluation of H and $\boldsymbol{P}$, and then use the Schrödinger equation to get rid of superfluous terms.

21.2 Klein's paradox

The commutation relations for the field operators $a(\boldsymbol{k})$ and $b^+(\boldsymbol{k})$ imply that the operator $\phi(\boldsymbol{x},t)$ (21.3) describes both particles and anti-particles simultaneously, and therefore the Klein-Gordon equation cannot support a single particle interpretation. This is also obvious from the charge and current operators (21.10) and (21.11), and the corresponding lack of a conserved probability density for Klein-Gordon particles. Klein's paradox provides a particularly neat illustration of the failure of single particle interpretations of relativistic wave equations.

Klein observed that using relativistic quantum fields to describe a relativistic particle running against a potential step yields results for the transmission and reflection probabilities which are incompatible with a single particle interpretation[3]. This observation can be explained by pair creation in strong fields

[3] O. Klein, Z. Phys. 53, 157 (1929). Klein actually discussed reflection and transmission of relativistic spin 1/2 fermions, which are described by the Dirac equation (21.31).

and the fact that relativistic fields describe both particles and anti-particles simultaneously. We will explain Klein's paradox for the Klein-Gordon field.
In the following we can neglect the y and z coordinates and deal only with the x and t coordinates. We are interested in a scalar particle of charge q scattered off a potential step of height V. The step is located at $x = 0$, and can be implemented through an electrostatic potential $\Phi(x)$,

$$V(x) = q\Phi(x) = -cqA_0(x) = V\Theta(x). \tag{21.15}$$

Minimal coupling then yields the free Klein-Gordon equation for $x < 0$, and[4]

$$(\hbar\partial_t + \mathrm{i}V)^2\,\phi - \hbar^2c^2\partial_x^2\phi + m^2c^4\phi = 0 \tag{21.16}$$

for $x > 0$.
A monochromatic solution without any apparent left moving component for $x > 0$ is (after omission of an irrelevant constant prefactor)

$$\phi(x,t) = \begin{cases} [\exp(\mathrm{i}kx) + \beta\exp(-\mathrm{i}kx)]\exp(-\mathrm{i}\omega t), & x < 0 \\ \theta\exp[\mathrm{i}(\kappa x - \omega t)], & x > 0. \end{cases} \tag{21.17}$$

The frequency follows from the solution of the Klein-Gordon equation in the two domains,

$$\omega = c\sqrt{k^2 + \frac{m^2c^2}{\hbar^2}} = \frac{V}{\hbar} \pm c\sqrt{\kappa^2 + \frac{m^2c^2}{\hbar^2}}. \tag{21.18}$$

It has to be the same in both regions for continuity of the wave function at $x = 0$.
The sign in the last equation of (21.18) depends on the sign of $\hbar\omega - V$. We apparently have to use the minus sign if and only if $\hbar\omega - V < 0$. Note that in our solution we always have $\hbar\omega \geq mc^2$.
Solving for κ yields

$$\kappa = \pm\frac{1}{\hbar}\sqrt{\frac{(\hbar\omega - V)^2}{c^2} - m^2c^2} \in \mathbb{R}, \quad (\hbar\omega - V)^2 > m^2c^4, \tag{21.19}$$

$$\kappa = \frac{\mathrm{i}}{\hbar}\sqrt{m^2c^2 - \frac{(\hbar\omega - V)^2}{c^2}} \in \mathrm{i}\mathbb{R}_+, \quad (\hbar\omega - V)^2 < m^2c^4. \tag{21.20}$$

However, we have to be careful with the sign in (21.19). The group velocity in $x > 0$ for $\hbar\omega + mc^2 < V$ (i.e. for the negative sign in (21.18)) is

$$\frac{d\omega}{d\kappa} = -c\frac{\hbar\kappa}{\sqrt{\hbar^2\kappa^2 + m^2c^2}},$$

[4] We cannot try to discuss motion of particles of mass m in the presence of a potential by simply including a scalar potential term in the form $\left(\hbar^2\partial_t^2 - \hbar^2c^2\partial_x^2 + m^2c^4\right)\phi = \Theta(x)V^2\phi$ in the Klein-Gordon equation. This would correspond to a local mass $M(x)c^2 = \sqrt{m^2c^4 - \Theta(x)V^2}$ rather than to a local potential, and yield tachyons in $x > 0$ for $V^2 > m^2c^4$.

i.e. we have to take the *negative* root for κ for $V > \hbar\omega + mc^2$ to ensure positive group velocity in the region $x > 0$. We can collect the results for κ in the equations

$$\begin{aligned}
&V < \hbar\omega - mc^2 : && \kappa = \tfrac{1}{\hbar}\sqrt{\tfrac{(\hbar\omega - V)^2}{c^2} - m^2c^2} \in \mathbb{R}_+,\\
&\hbar\omega - mc^2 < V < \hbar\omega + mc^2 : && \kappa = \tfrac{\mathrm{i}}{\hbar}\sqrt{m^2c^2 - \tfrac{(\hbar\omega - V)^2}{c^2}} \in \mathrm{i}\mathbb{R}_+,\\
&V > \hbar\omega + mc^2 : && \kappa = -\tfrac{1}{\hbar}\sqrt{\tfrac{(\hbar\omega - V)^2}{c^2} - m^2c^2} \in \mathbb{R}_-.
\end{aligned}$$

The current density $j = \mathrm{i}qc^2(\partial_x\phi^+ \cdot \phi - \phi^+ \cdot \partial_x\phi)$ is

$$\begin{aligned}
&j = 2qc^2k(1 - |\beta|^2), && x < 0,\\
&j = 2qc^2\kappa|\theta|^2, && x > 0,\ \kappa \in \mathbb{R},\\
&j = 0, && x > 0,\ \kappa \in \mathrm{i}\mathbb{R}.
\end{aligned} \tag{21.21}$$

Note that in $x > 0$ we have $j/q < 0$ if $V > \hbar\omega + mc^2$, in spite of the fact of positive group velocity in the region. Since charges q cannot move to the left in $x > 0$, this means that the negative value of j/q in $x > 0$ for $V > \hbar\omega + mc^2$ must correspond to right moving charges $-q$. We will see that this arises as a consequence of the generation of anti-particles near the potential step for $V > \hbar\omega + mc^2$.
The junction conditions

$$1 + \beta = \theta, \quad k(1 - \beta) = \kappa\theta \tag{21.22}$$

yield

$$\beta = \frac{k - \kappa}{k + \kappa}, \quad \theta = \frac{2k}{k + \kappa},$$

and the corresponding reflection and transmission coefficients are

$$\begin{aligned}
R &= |\beta|^2 = \frac{k^2 + |\kappa|^2 - 2k\Re\kappa}{k^2 + |\kappa|^2 + 2k\Re\kappa},\\
T &= \frac{\Re\kappa}{k}|\theta|^2 = \frac{4k\Re\kappa}{k^2 + |\kappa|^2 + 2k\Re\kappa} = 1 - R.
\end{aligned}$$

This yields the following behavior of the reflection coefficient as a function of V:

$$\begin{aligned}
&-\infty < V \le 0 : && \infty > \kappa \ge k, && 1 > R \ge 0, && 0 < T \le 1,\\
&0 \le V \le \hbar\omega - mc^2 : && k \ge \kappa \ge 0, && 0 \le R \le 1, && 1 \ge T \ge 0,\\
&\hbar\omega - mc^2 < V < \hbar\omega + mc^2 : && \kappa \in \mathrm{i}\mathbb{R}_+, && R = 1, && T = 0,\\
&\hbar\omega + mc^2 \le V \le 2\hbar\omega : && 0 \ge \kappa \ge -k, && 1 \le R \le \infty, && 0 \ge T \ge -\infty,\\
&2\hbar\omega \le V < \infty : && -k \ge \kappa > -\infty, && \infty \ge R > 1, && -\infty \le T < 0.
\end{aligned} \tag{21.23}$$

For an explanation of the unexpected result $R > 1$ for $V > \hbar\omega + mc^2 \geq 2mc^2$, recall that the solution for $V > \hbar\omega + mc^2$ in $x > 0$ has $\kappa < 0$. If we write the solution as

$$\phi(x,t) = \theta \exp[-\mathrm{i}(-\kappa x + \omega t)], \quad x > 0, \tag{21.24}$$

and compare with the anti-particle contribution to the free solution (21.3), we recognize the solution in the region $x > 0$ as an anti-particle solution with momentum $\hbar\kappa' = -\hbar\kappa > 0$ and energy

$$E_{\overline{p}} = -\hbar\omega < 0, \quad mc^2 - V \leq E_{\overline{p}} \leq -mc^2. \tag{21.25}$$

This is acceptable, because the anti-particle has charge $-q$ and therefore experiences a potential $U = -V$ in the region $x > 0$. Further support for this energy assignment for the anti-particles comes from the equality for the kinetic+rest energy of the anti-particles,

$$K_{\overline{p}} = c\sqrt{\hbar^2\kappa^2 + m^2c^2} = V - \hbar\omega, \quad mc^2 \leq K_{\overline{p}} \leq V - mc^2. \tag{21.26}$$

We expect $E_{\overline{p}} = K_{\overline{p}} - V$ at least in the non-relativistic limit for the anti-particles.

The anti-particles move to the right, $d(-\omega)/d(-\kappa) > 0$, and yield a negative particle current density $j/q \propto -q\kappa'/q = -\kappa' < 0$ due to the opposite charge. We therefore get $R > 1$ and $T < 0$ for $V - \hbar\omega > mc^2$ due to pair creation. The generated particles move to the left because they are repelled by the potential $V > mc^2 + \hbar\omega$. They add to the reflected particle in $x < 0$ to generate a formal reflection coefficient $R > 1$. The anti-particles move to the right because they can only move in the attractive potential $-V$ in $x > 0$. The movement of charges $-q$ to the right generates a negative apparent transmission coefficient $T = j_{x>0}/j_{in} < 0$.

Please note that the last two lines in equation (21.23) do *not* say that extremely large potentials $V \gg 2mc^2$ are less efficient for pair creation. They only state that a potential $V > 2mc^2$ is particularly efficient for generation of particle–anti-particle pairs with energies $E_p = -E_{\overline{p}} = \hbar\omega = V/2$.

The conclusion in a nutshell is that if we wish to calculate scattering in the potential $V > 2mc^2$ for incident particles with energies in the pair creation region $mc^2 \leq \hbar\omega \leq V - mc^2$, then the ongoing pair creation will yield the seemingly paradoxical results $R > 1$ and $T = 1 - R < 0$ see Figure 21.1.

Please note that a more satisfactory discussion of energetics of the problem would also have to take into account the dynamics of the electromagnetic field $\Phi = V/q$, and then use the Hamiltonian density (21.117) of quantum electrodynamics with scalar matter. This would also imply an additional energy cost for separating the oppositely charged particles and anti-particles. The potential V would therefore decay due to pair creation until it satisfies the condition $V \leq 2mc^2$, when pair creation would seize and the standard single particle results $0 \leq T = 1 - R \leq 1$ apply for incident particles with any energy, or the potential would have to be maintained through an external energy source.

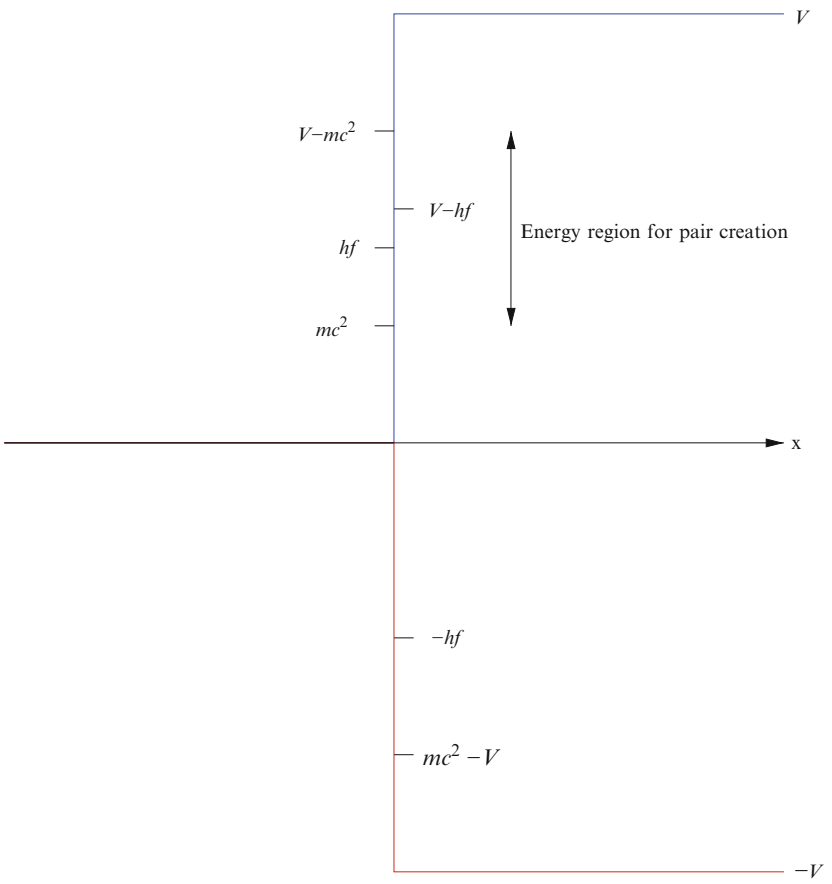


Figure 21.1: Particles of charge q experience the potential V for $x > 0$, while anti-particles with charge $-q$ experience the potential $-V$. If the potential satisfies $V > 2mc^2$, it can produce particles with energy E_p, $mc^2 \leq E_p = hf \leq V - mc^2$, in the region $x < 0$ and anti-particles with energy $E_{\overline{p}} = -hf$, $mc^2 - V \leq E_{\overline{p}} \leq -mc^2$, in the region $x > 0$. Pair creation is most efficient for $E_p = -E_{\overline{p}} = V/2$.

21.3 The Dirac equation

We have seen in equation (21.10) that the conserved charge of the complex Klein-Gordon field does not yield a conserved probability, and therefore has no single particle interpretation. This had motivated Paul Dirac in 1928 to

propose a relativistic wave equation which is linear in the derivatives[5],

$$\mathrm{i}\hbar\gamma^\mu\partial_\mu\Psi(x) - mc\Psi(x) = 0. \tag{21.27}$$

Since the relativistic dispersion relation $p^2 + m^2c^2 = 0$ implies that the field Ψ should still satisfy the Klein-Gordon equation, equation (21.27) should imply the Klein-Gordon equation. Applying the operator $\mathrm{i}\hbar\gamma^\mu\partial_\mu + mc$ yields

$$-\hbar^2\gamma^\mu\gamma^\nu\partial_\mu\partial_\nu\Psi(x) - m^2c^2\Psi(x) = 0.$$

This is the Klein-Gordon equation if the coefficients γ^μ can be chosen to satisfy

$$\{\gamma^\mu, \gamma^\nu\} = -2\eta^{\mu\nu}. \tag{21.28}$$

In four dimensions, equation (21.28) has an up to equivalence transformations unique solution in terms of (4×4)-matrices (see Appendix G for the relevant proofs and for the construction of γ matrices in d spacetime dimensions). The Dirac basis for γ matrices is

$$\gamma_0 = \begin{pmatrix} -\underline{1} & \underline{0} \\ \underline{0} & \underline{1} \end{pmatrix}, \quad \gamma_i = \begin{pmatrix} \underline{0} & \underline{\sigma}_i \\ -\underline{\sigma}_i & \underline{0} \end{pmatrix}, \tag{21.29}$$

where the of the (4×4)-matrices are expressed in terms of (2×2)-matrices. Another often used basis is the Weyl basis:

$$\gamma_0 = \begin{pmatrix} \underline{0} & \underline{1} \\ \underline{1} & \underline{0} \end{pmatrix}, \quad \gamma_i = \begin{pmatrix} \underline{0} & \underline{\sigma}_i \\ -\underline{\sigma}_i & \underline{0} \end{pmatrix}. \tag{21.30}$$

The two bases are related by the orthogonal transformation

$$\gamma^\mu_W = \frac{1}{2}\begin{pmatrix} \underline{1} & \underline{1} \\ -\underline{1} & \underline{1} \end{pmatrix} \cdot \gamma^\mu_D \cdot \begin{pmatrix} \underline{1} & -\underline{1} \\ \underline{1} & \underline{1} \end{pmatrix},$$

$$\gamma^\mu_D = \frac{1}{2}\begin{pmatrix} \underline{1} & -\underline{1} \\ \underline{1} & \underline{1} \end{pmatrix} \cdot \gamma^\mu_W \cdot \begin{pmatrix} \underline{1} & \underline{1} \\ -\underline{1} & \underline{1} \end{pmatrix}.$$

The Dirac equation with minimal photon coupling

$$\gamma^\mu(\mathrm{i}\hbar\partial_\mu + qA_\mu)\Psi(x) - mc\Psi(x) = 0 \tag{21.31}$$

follows from the Lagrange density of quantum electrodynamics,

$$\mathcal{L} = c\overline{\Psi}\left[\gamma^\mu(\mathrm{i}\hbar\partial_\mu + qA_\mu) - mc\right]\Psi - \frac{1}{4\mu_0}F_{\mu\nu}F^{\mu\nu}, \quad \overline{\Psi} = \Psi^+\gamma^0. \tag{21.32}$$

[5] P.A.M. Dirac, Proc. Roy. Soc. London A 117, 610 (1928). Dirac's relativistic wave equation was a great success, but like every relativistic wave equation, it also does not yield a single particle interpretation. It immediately proved itself by explaining the anomalous magnetic moment of the electron and the fine structure of spectral lines, and by predicting positrons.

The conserved current density for the phase invariance

$$\Psi' = \exp\left(\mathrm{i}\frac{q}{\hbar}\alpha\right)\Psi$$

is

$$j^\mu = cq\overline{\Psi}\gamma^\mu\Psi, \quad \varrho = j^0/c = q\Psi^+\Psi, \quad \boldsymbol{j} = cq\overline{\Psi}\boldsymbol{\gamma}\Psi. \tag{21.33}$$

Variation of (21.32) with respect to the vector potential shows that j^μ appears as the source term in Maxwell's equations,

$$\partial_\mu F^{\mu\nu} = -\mu_0 j^\nu.$$

Solutions of the free Dirac equation

We temporarily set $\hbar = 1$ and $c = 1$ for the construction of the general solution of the free Dirac equation.
Substitution of the Fourier *ansatz*

$$\Psi(x) = \int \frac{d^4p}{(2\pi)^2}\,\Psi(p)\exp(\mathrm{i}p\cdot x)$$

into (21.27) yields the equation

$$(\gamma^\mu p_\mu + m)\Psi(p) = 0. \tag{21.34}$$

We can use any representation of the γ matrices to find

$$\det(\gamma^\mu p_\mu + m) = (m^2 + p^2)^2 = (m^2 + \boldsymbol{p}^2 - E^2)^2 = (E^2(\boldsymbol{p}) - E^2)^2,$$

i.e. the solutions of (21.34) must have the form

$$\Psi(p) = \sqrt{\frac{\pi}{E(\boldsymbol{p})}}u(\boldsymbol{p})\delta(E - E(\boldsymbol{p})) + \sqrt{\frac{\pi}{E(\boldsymbol{p})}}v(-\boldsymbol{p})\delta(E + E(\boldsymbol{p}))$$

with $E(\boldsymbol{p}) = \sqrt{\boldsymbol{p}^2 + m^2}$. The normalization factors are included for convenience.
To find the eigenspinors $u(\boldsymbol{p})$, $v(-\boldsymbol{p})$, we observe

$$(\gamma^\mu p_\mu + m)(m - \gamma^\mu p_\mu) = m^2 + p^2,$$

i.e. the columns $\zeta_{i\pm}(\boldsymbol{p})$ of the matrix $(m - \gamma^\mu p_\mu)_{E=\pm E(\boldsymbol{p})}$ solve the equation (21.34).
We initially use a Dirac basis (21.29) for the γ matrices. A suitable basis for the general solution of the free Dirac equation is then given by the spin basis in the Dirac representation,

$$\begin{aligned} u(\boldsymbol{p}, \tfrac{1}{2}) = u_\uparrow(\boldsymbol{p}) &= \frac{1}{\sqrt{E(\boldsymbol{p}) + m}}\zeta_{1+}(\boldsymbol{p}) \\ &= \frac{1}{\sqrt{E(\boldsymbol{p}) + m}}\begin{pmatrix} E(\boldsymbol{p}) + m \\ 0 \\ p_3 \\ p_+ \end{pmatrix}, \end{aligned} \tag{21.35}$$

$$u(\boldsymbol{p},-\tfrac{1}{2}) = u_{\downarrow}(\boldsymbol{p}) = \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\zeta_{2+}(\boldsymbol{p})$$
$$= \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\begin{pmatrix} 0 \\ E(\boldsymbol{p})+m \\ p_- \\ -p_3 \end{pmatrix}, \tag{21.36}$$

$$v(-\boldsymbol{p},-\tfrac{1}{2}) = v_{\downarrow}(-\boldsymbol{p}) = \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\zeta_{3-}(\boldsymbol{p})$$
$$= \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\begin{pmatrix} -p_3 \\ -p_+ \\ E(\boldsymbol{p})+m \\ 0 \end{pmatrix}, \tag{21.37}$$

$$v(-\boldsymbol{p},\tfrac{1}{2}) = v_{\uparrow}(-\boldsymbol{p}) = \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\zeta_{4-}(\boldsymbol{p})$$
$$= \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\begin{pmatrix} -p_- \\ p_3 \\ 0 \\ E(\boldsymbol{p})+m \end{pmatrix}. \tag{21.38}$$

It is also convenient to express these spinors in terms of the 2-spinors

$$\chi_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

in the form

$$u_{\uparrow}(\boldsymbol{p}) = \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\begin{pmatrix} (E(\boldsymbol{p})+m)\chi_{\uparrow} \\ (\boldsymbol{p}\cdot\underline{\boldsymbol{\sigma}})\cdot\chi_{\uparrow} \end{pmatrix},$$

$$u_{\downarrow}(\boldsymbol{p}) = \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\begin{pmatrix} (E(\boldsymbol{p})+m)\chi_{\downarrow} \\ (\boldsymbol{p}\cdot\underline{\boldsymbol{\sigma}})\cdot\chi_{\downarrow} \end{pmatrix},$$

$$v_{\downarrow}(\boldsymbol{p}) = \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\begin{pmatrix} (\boldsymbol{p}\cdot\underline{\boldsymbol{\sigma}})\cdot\chi_{\uparrow} \\ (E(\boldsymbol{p})+m)\chi_{\uparrow} \end{pmatrix},$$

$$v_{\uparrow}(\boldsymbol{p}) = \frac{1}{\sqrt{E(\boldsymbol{p})+m}}\begin{pmatrix} (\boldsymbol{p}\cdot\underline{\boldsymbol{\sigma}})\cdot\chi_{\downarrow} \\ (E(\boldsymbol{p})+m)\chi_{\downarrow} \end{pmatrix}.$$

The general solution of the free Dirac equation then has the form

$$\Psi(x) = \frac{1}{\sqrt{2\pi}^3}\int\frac{d^3\boldsymbol{p}}{\sqrt{2E(\boldsymbol{p})}}\sum_{s\in\{\downarrow,\uparrow\}}\big[b_s(\boldsymbol{p})u_s(\boldsymbol{p})\exp(\mathrm{i}p\cdot x)$$
$$+d_s^+(\boldsymbol{p})v_s(\boldsymbol{p})\exp(-\mathrm{i}p\cdot x)\big], \tag{21.39}$$

where $p^0 = E(\boldsymbol{p})$ is understood: $p\cdot x = \boldsymbol{p}\cdot\boldsymbol{x} - E(\boldsymbol{p})t$.

Some useful algebraic properties of the spinors (21.35-21.38) occur frequently in the calculations of cross sections and other observables,

$$u^+(\boldsymbol{p},s)\cdot u(\boldsymbol{p},s') = 2E(\boldsymbol{p})\delta_{ss'}, \quad v^+(\boldsymbol{p},s)\cdot v(\boldsymbol{p},s') = 2E(\boldsymbol{p})\delta_{ss'}, \tag{21.40}$$

$$u^+(\boldsymbol{p},s)\cdot v(-\boldsymbol{p},s') = 0, \quad \overline{u}(\boldsymbol{p},s)\cdot v(\boldsymbol{p},s') = 0, \tag{21.41}$$

$$\overline{u}(\boldsymbol{p},s)\cdot u(\boldsymbol{p},s') = 2m\delta_{ss'}, \quad \overline{v}(\boldsymbol{p},s)\cdot v(\boldsymbol{p},s') = -2m\delta_{ss'}, \tag{21.42}$$

$$\begin{aligned}&\overline{u}(\boldsymbol{p},+)\cdot v(-\boldsymbol{p},-) = -2p_3, \quad \overline{u}(\boldsymbol{p},+)\cdot v(-\boldsymbol{p},+) = -2p_-,\\ &\overline{u}(\boldsymbol{p},-)\cdot v(-\boldsymbol{p},-) = -2p_+, \quad \overline{u}(\boldsymbol{p},-)\cdot v(-\boldsymbol{p},+) = 2p_3.\end{aligned} \tag{21.43}$$

The following equations contain 4×4 unit matrices on the right hand sides,

$$\sum_s u(\boldsymbol{p},s)u^+(\boldsymbol{p},s) + \sum_s v(-\boldsymbol{p},s)v^+(-\boldsymbol{p},s) = 2E(\boldsymbol{p})1, \tag{21.44}$$

$$\sum_s u(\boldsymbol{p},s)\overline{u}(\boldsymbol{p},s) = m1 - \gamma^\mu p_\mu\Big|_{E=E(\boldsymbol{p})}, \tag{21.45}$$

$$\sum_s u(-\boldsymbol{p},s)\overline{u}(-\boldsymbol{p},s) = m1 + \gamma^\mu p_\mu\Big|_{E=-E(\boldsymbol{p})}, \tag{21.46}$$

$$\sum_s v(\boldsymbol{p},s)\overline{v}(\boldsymbol{p},s) = -m1 - \gamma^\mu p_\mu\Big|_{E=E(\boldsymbol{p})}, \tag{21.47}$$

$$\sum_s v(-\boldsymbol{p},s)\overline{v}(-\boldsymbol{p},s) = -m1 + \gamma^\mu p_\mu\Big|_{E=-E(\boldsymbol{p})}. \tag{21.48}$$

It is actually clumsy to write down unit matrices when their presence is clear from the context, and the action e.g. of the scalar $E(\boldsymbol{p})$ on a 4-spinor Ψ has the same effect as the matrix $E(\boldsymbol{p})1$. Therefore we will adopt the general practice of not writing down 4×4 unit matrices explicitly.

Calculations involving 4-spinors are often conveniently carried out with $\hbar = 1$ and $c = 1$, and restoration of the constants is usually only done in the final results from the requirement of correct units. For completeness I would also like to give the general solution of the free Dirac equation with the constants $\hbar$ and c restored. We can choose the basic spinors (21.35-21.38) to have units of square roots of energy, e.g.

$$u_\uparrow(\boldsymbol{k}) = \frac{1}{\sqrt{E(\boldsymbol{k})+mc^2}}\begin{pmatrix} E(\boldsymbol{k})+mc^2 \\ 0 \\ \hbar c k_3 \\ \hbar c k_+ \end{pmatrix},$$

and the solution (21.39) is

$$\begin{aligned}\Psi(x) = \frac{1}{\sqrt{2\pi}^3}\int \frac{d^3\boldsymbol{k}}{\sqrt{2E(\boldsymbol{k})}} \sum_{s\in\{\downarrow,\uparrow\}} \big[&b_s(\boldsymbol{k})u_s(\boldsymbol{k})\exp(\mathrm{i}k\cdot x)\\ &+d_s^+(\boldsymbol{k})v_s(\boldsymbol{k})\exp(-\mathrm{i}k\cdot x)\big]\end{aligned} \tag{21.49}$$

with $k\cdot x \equiv \boldsymbol{k}\cdot\boldsymbol{x} - \omega(\boldsymbol{k})t$. In these conventions the Dirac field has the same dimensions length$^{-3/2}$ as the Schrödinger field. The free field $\Psi(x)$ also describes the freely evolving field operator $\Psi_D(x)$ in the interaction picture.

Charge operators and quantization of the Dirac field

We can apply the results from Section 16.2 to calculate the energy and momentum operator for the Dirac field. The free Dirac Lagrangian

$$\mathcal{L} = c\overline{\Psi}\left(\mathrm{i}\hbar\gamma^\mu\partial_\mu - mc\right)\Psi \tag{21.50}$$

yields the positive definite normal ordered Hamiltonian

$$\begin{aligned} H &= \int d^3\boldsymbol{x}\, c\overline{\Psi}(\boldsymbol{x},t)\left(mc - \mathrm{i}\hbar\boldsymbol{\gamma}\cdot\boldsymbol{\nabla}\right)\Psi(\boldsymbol{x},t) \\ &= \int d^3\boldsymbol{k}\,\hbar\omega(\boldsymbol{k})\sum_{s\in\{\downarrow,\uparrow\}}\left[b_s^+(\boldsymbol{k})b_s(\boldsymbol{k}) + d_s^+(\boldsymbol{k})d_s(\boldsymbol{k})\right], \end{aligned} \tag{21.51}$$

but only if we assume anti-commutation properties of the d_s and d_s^+ operators. The normal ordered momentum operator is then

$$\begin{aligned} \boldsymbol{P} &= \int d^3\boldsymbol{x}\,\Psi^+(\boldsymbol{x},t)\frac{\hbar}{\mathrm{i}}\boldsymbol{\nabla}\Psi(\boldsymbol{x},t) \\ &= \int d^3\boldsymbol{k}\,\hbar\boldsymbol{k}\sum_{s\in\{\downarrow,\uparrow\}}\left[b_s^+(\boldsymbol{k})b_s(\boldsymbol{k}) + d_s^+(\boldsymbol{k})d_s(\boldsymbol{k})\right]. \end{aligned} \tag{21.52}$$

The electromagnetic current density (21.33) yields the charge operator

$$\begin{aligned} Q &= q\int d^3\boldsymbol{x}\,\Psi^+(\boldsymbol{x},t)\Psi(\boldsymbol{x},t) \\ &= q\int d^3\boldsymbol{k}\sum_{s\in\{\downarrow,\uparrow\}}\left[b_s^+(\boldsymbol{k})b_s(\boldsymbol{k}) - d_s^+(\boldsymbol{k})d_s(\boldsymbol{k})\right]. \end{aligned} \tag{21.53}$$

The normalization in equation (21.39) has been chosen such that the quantization condition

$$\{\Psi_\alpha(\boldsymbol{x},t), {\Psi_\beta}^+(\boldsymbol{x}',t)\} = \delta_{\alpha\beta}\delta(\boldsymbol{x}-\boldsymbol{x}')$$

for the components of $\Psi(x)$ yields

$$\{b(\boldsymbol{k},s), b^+(\boldsymbol{k}',s')\} = \delta_{ss'}\delta(\boldsymbol{k}-\boldsymbol{k}'), \quad \{d(\boldsymbol{k},s), d^+(\boldsymbol{k}',s')\} = \delta_{ss'}\delta(\boldsymbol{k}-\boldsymbol{k}'),$$

with the other anti-commutators vanishing. The equations (21.51-21.53) then imply that the operator $b^+(\boldsymbol{k},s)$ creates a fermion of mass m, momentum $\hbar\boldsymbol{k}$ and charge q, while $d^+(\boldsymbol{k},s)$ creates a particle with the same mass and momentum, but opposite charge $-q$.
For an explanation of the spin labels of the spinors $u(\boldsymbol{k},\pm\frac{1}{2})$, we notice that the spin operators corresponding to the rotation generators

$$M_i = -\mathrm{i}L_i = \frac{1}{2}\epsilon_{ijk}M_{jk}$$

are both in the Dirac and in the Weyl representation given by

$$S_i = \frac{\hbar}{2}\epsilon_{ijk}S_{jk} = \frac{\mathrm{i}\hbar}{4}\epsilon_{ijk}\gamma_j\gamma_k = \frac{\hbar}{2}\begin{pmatrix}\underline{\sigma}_i & 0\\ 0 & \underline{\sigma}_i\end{pmatrix}, \tag{21.54}$$

see Appendix H for an explanation of generators of Lorentz boosts and rotations for Dirac spinors.
Equation (21.54) implies that the rest frame spinors $u(\mathbf{0}, \pm\frac{1}{2})$ transform under rotations around the z axis as spinors with z-component of spin $\hbar s = \pm\hbar/2$. For an explanation of the spin labels of the spinors $v(\boldsymbol{p}, \pm\frac{1}{2})$, we have to look at charge conjugation. Both in the Dirac and the Weyl representation of γ matrices we have

$$\gamma_\mu^* = \gamma_2\gamma_\mu\gamma_2.$$

Therefore complex conjugation of the Dirac equation

$$[\mathrm{i}\gamma^\mu\partial_\mu + q\gamma^\mu A_\mu(x) - m]\Psi(x) = 0,$$

followed by multiplication with $\mathrm{i}\gamma_2$ from the left yields

$$[\mathrm{i}\gamma^\mu\partial_\mu - q\gamma^\mu A_\mu(x) - m]\Psi^c(x) = 0$$

with the *charge conjugate* field

$$\Psi^c(x) = \mathrm{i}\gamma_2\Psi^*(x).$$

In particular, we have

$$v^c(\boldsymbol{k}, \tfrac{1}{2}) = \mathrm{i}\gamma_2 v^*(\boldsymbol{k}, \tfrac{1}{2}) = u(\boldsymbol{k}, \tfrac{1}{2})$$

and

$$v^c(\boldsymbol{k}, -\tfrac{1}{2}) = \mathrm{i}\gamma_2 v^*(\boldsymbol{k}, -\tfrac{1}{2}) = -u(\boldsymbol{k}, -\tfrac{1}{2}),$$

i.e. the negative energy spinors for charge q, momentum $\hbar\boldsymbol{k}$ and spin projection $\hbar s$ correspond to positive energy spinors for charge $-q$, momentum $\hbar\boldsymbol{k}$ and spin projection $\hbar s$.

21.4 Energy-momentum tensor for quantum electrodynamics

We use the symmetrized form of the QED Lagrangian (21.32),

$$\mathcal{L} = c\overline{\Psi}\left[\gamma^\mu\left(\frac{\mathrm{i}\hbar}{2}\overset{\leftrightarrow}{\partial}_\mu + qA_\mu\right) - mc\right]\Psi - \frac{1}{4\mu_0}F_{\mu\nu}F^{\mu\nu}. \tag{21.55}$$

This yields according to (16.14) a conserved energy-momentum tensor

$$\begin{aligned}\Theta_\mu{}^\nu &= \eta_\mu{}^\nu \mathcal{L} - \partial_\mu \overline{\Psi} \frac{\partial \mathcal{L}}{\partial(\partial_\nu \overline{\Psi})} - \partial_\mu \Psi \frac{\partial \mathcal{L}}{\partial(\partial_\nu \Psi)} - \partial_\mu A_\lambda \frac{\partial \mathcal{L}}{\partial(\partial_\nu A_\lambda)} \\ &= \eta_\mu{}^\nu \left(c\overline{\Psi} \left[\gamma^\lambda \left(\frac{\mathrm{i}\hbar}{2} \overset{\leftrightarrow}{\partial_\lambda} + qA_\lambda \right) - mc \right] \Psi - \frac{1}{4\mu_0} F_{\kappa\lambda} F^{\kappa\lambda} \right) \\ &\quad - \frac{\mathrm{i}\hbar}{2} c\overline{\Psi}\gamma^\nu \overset{\leftrightarrow}{\partial_\mu} \Psi + \frac{1}{\mu_0} \partial_\mu A_\lambda F^{\nu\lambda}.\end{aligned}$$

According to the results of Section 16.2, this gives us on-shell conserved charges, i.e. we can use the equations of motion to simplify this expression. The Dirac equation then implies

$$\Theta_\mu{}^\nu = -\frac{\mathrm{i}\hbar}{2} c\overline{\Psi}\gamma^\nu \overset{\leftrightarrow}{\partial_\mu} \Psi + \frac{1}{\mu_0} \partial_\mu A_\lambda F^{\nu\lambda} - \frac{1}{4\mu_0} \eta_\mu{}^\nu F_{\kappa\lambda} F^{\kappa\lambda}.$$

We can also add the identically conserved improvement term

$$\begin{aligned}-\frac{1}{\mu_0} \partial_\lambda \left(A_\mu F^{\nu\lambda} \right) &= -\frac{1}{\mu_0} \partial_\lambda A_\mu F^{\nu\lambda} - \frac{1}{\mu_0} A_\mu \partial_\lambda F^{\nu\lambda} \\ &= -\frac{1}{\mu_0} \partial_\lambda A_\mu F^{\nu\lambda} - qcA_\mu \overline{\Psi}\gamma^\nu \Psi,\end{aligned}$$

where Maxwell's equations

$$\partial_\mu F^{\mu\nu} = -\mu_0 qc\overline{\Psi}\gamma^\nu \Psi$$

have been used. This yields the gauge invariant tensor

$$\begin{aligned}t_\mu{}^\nu &= \Theta_\mu{}^\nu - \frac{1}{\mu_0} \partial_\lambda \left(A_\mu F^{\nu\lambda} \right) \\ &= -\frac{\mathrm{i}\hbar}{2} c\overline{\Psi}\gamma^\nu \overset{\leftrightarrow}{\partial_\mu} \Psi - qc\overline{\Psi}\gamma^\nu A_\mu \Psi + \frac{1}{\mu_0} F_{\mu\lambda} F^{\nu\lambda} - \eta_\mu{}^\nu \frac{1}{4\mu_0} F_{\kappa\lambda} F^{\kappa\lambda}. \quad (21.56)\end{aligned}$$

However, we can go one step further and replace $t_\mu{}^\nu$ with a symmetric energy-momentum tensor. The divergence of the spinor term in $t_\mu{}^\nu$ is

$$\partial_\nu \left(\frac{\mathrm{i}\hbar}{2} \overline{\Psi}\gamma^\nu \overset{\leftrightarrow}{\partial_\mu} \Psi + q\overline{\Psi}\gamma^\nu A_\mu \Psi \right) = -q\overline{\Psi} F_{\mu\nu} \gamma^\nu \Psi,$$

where again the Dirac equation was used.
The symmetrization of $t_\mu{}^\nu$ also involves the commutators of γ matrices,

$$S_{\mu\nu} = \frac{\mathrm{i}}{4} [\gamma_\mu, \gamma_\nu] = \gamma_0 \cdot S^+_{\mu\nu} \cdot \gamma_0. \quad (21.57)$$

Since we can write a product always as a sum of an anti-commutator and a commutator, we have

$$\gamma_\mu \cdot \gamma_\nu = -\eta_{\mu\nu} - 2\mathrm{i} S_{\mu\nu}, \quad (21.58)$$

and the commutators also satisfy[6]

$$\eta_{\mu\alpha}\gamma_\beta - \eta_{\mu\beta}\gamma_\alpha + \mathrm{i}[S_{\alpha\beta}, \gamma_\mu] = 0. \tag{21.59}$$

Equations (21.57-21.59) together with

$$\begin{aligned}\hbar^2\partial^2\Psi &= \mathrm{i}\hbar\gamma^\mu\partial_\mu\left(mc\Psi - q\gamma^\nu A_\nu\Psi\right)\\ &= \mathrm{i}\hbar q\left[\partial_\mu\left(A^\mu\Psi\right) + 2\mathrm{i}S^{\mu\nu}\partial_\mu\left(A_\nu\Psi\right)\right] + mc\left[mc\Psi - q\gamma^\nu A_\nu\Psi\right],\end{aligned}$$

imply also

$$\partial_\nu\left(\frac{\mathrm{i}\hbar}{2}\overline{\Psi}\gamma_\mu\overset{\leftrightarrow}{\partial^\nu}\Psi + q\overline{\Psi}\gamma_\mu A^\nu\Psi\right) = -q\overline{\Psi}F_{\mu\nu}\gamma^\nu\Psi.$$

Therefore the local conservation law $\partial_\nu T_\mu{}^\nu = 0$ also holds for the symmetrized energy-momentum tensor

$$\begin{aligned}T_\mu{}^\nu = &-\frac{c}{2}\overline{\Psi}\left[\frac{\mathrm{i}\hbar}{2}\gamma^\nu\overset{\leftrightarrow}{\partial_\mu} + \frac{\mathrm{i}\hbar}{2}\gamma_\mu\overset{\leftrightarrow}{\partial^\nu} + q\gamma^\nu A_\mu + q\gamma_\mu A^\nu\right]\Psi\\ &+\frac{1}{\mu_0}F_{\mu\lambda}F^{\nu\lambda} - \eta_\mu{}^\nu\frac{1}{4\mu_0}F_{\kappa\lambda}F^{\kappa\lambda}.\end{aligned} \tag{21.60}$$

This yields in particular the Hamiltonian density

$$\begin{aligned}\mathcal{H} &= -T_0{}^0 = c\Psi^+\left[\frac{\mathrm{i}\hbar}{2}\overset{\leftrightarrow}{\partial_0} + qA_0\right]\Psi + \frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2\\ &= c\overline{\Psi}\left[mc - \frac{\mathrm{i}\hbar}{2}\boldsymbol{\gamma}\cdot\overset{\leftrightarrow}{\boldsymbol{\nabla}} - q\boldsymbol{\gamma}\cdot\boldsymbol{A}\right]\Psi + \frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2,\end{aligned} \tag{21.61}$$

and the momentum density with components $\mathcal{P}_i = T_i{}^0/c$,

$$\boldsymbol{\mathcal{P}} = \frac{1}{2}\Psi^+\left[\frac{\hbar}{2\mathrm{i}}\overset{\leftrightarrow}{\boldsymbol{\nabla}} - q\boldsymbol{A}\right]\Psi + \frac{1}{2}\overline{\Psi}\boldsymbol{\gamma}\left[\frac{\mathrm{i}\hbar}{2}\overset{\leftrightarrow}{\partial_0} + qA_0\right]\Psi + \epsilon_0\boldsymbol{E}\times\boldsymbol{B}. \tag{21.62}$$

This momentum density differs on-shell by a curl $\boldsymbol{\nabla}\times(\Psi^+\cdot\boldsymbol{S}\cdot\Psi)/2$ (with the vector of 4×4 spin matrices $\boldsymbol{S}$ (21.54)) from the momentum density that also follows directly from the tensor (21.56),

$$\boldsymbol{\mathcal{P}} = \Psi^+\left[\frac{\hbar}{2\mathrm{i}}\overset{\leftrightarrow}{\boldsymbol{\nabla}} - q\boldsymbol{A}\right]\Psi + \epsilon_0\boldsymbol{E}\times\boldsymbol{B}. \tag{21.63}$$

In materials science it is convenient to explicitly disentangle the contributions from Coulomb and photon terms in Coulomb gauge $\boldsymbol{\nabla}\cdot\boldsymbol{A} = 0$. We split the electric field components in Coulomb gauge according to

$$\boldsymbol{E}_\parallel = -\boldsymbol{\nabla}\Phi \tag{21.64}$$

[6]The commutators $S_{\mu\nu}$ provide the spinor representation of the generators of Lorentz transformations. Furthermore, equation (21.59) is the invariance of the γ matrices under Lorentz transformations, see Appendix H.

and

$$\boldsymbol{E}_\perp = -\frac{\partial \boldsymbol{A}}{\partial t}. \tag{21.65}$$

The equation for the electrostatic potential decouples from the vector potential,

$$\Delta\Phi = -\frac{q}{\epsilon_0}\Psi^+\Psi,$$

and is solved by

$$\Phi(\boldsymbol{x},t) = \frac{q}{4\pi\epsilon_0}\int d^3\boldsymbol{x}'\,\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\Psi^+(\boldsymbol{x}',t)\Psi(\boldsymbol{x}',t).$$

Furthermore, the two components of the electric field are orthogonal in Coulomb gauge,

$$\begin{aligned}\int d^3\boldsymbol{x}\,\boldsymbol{E}_\parallel(\boldsymbol{x},t)\cdot\boldsymbol{E}_\perp(\boldsymbol{x},t) &= \int d^3\boldsymbol{k}\,\boldsymbol{E}_\parallel(\boldsymbol{k},t)\cdot\boldsymbol{E}_\perp(-\boldsymbol{k},t)\\ &= -\int d^3\boldsymbol{x}\,\Phi(\boldsymbol{x},t)\frac{\partial}{\partial t}\boldsymbol{\nabla}\cdot\boldsymbol{A}(\boldsymbol{x},t) = 0,\end{aligned} \tag{21.66}$$

and the contribution from $\boldsymbol{E}_\parallel$ to the Hamiltonian is

$$\begin{aligned}H_C &= \frac{\epsilon_0}{2}\int d^3\boldsymbol{x}\,\boldsymbol{E}_\parallel^2(\boldsymbol{x},t) = -\frac{\epsilon_0}{2}\int d^3\boldsymbol{x}\,\Phi(\boldsymbol{x},t)\Delta\Phi(\boldsymbol{x},t)\\ &= \frac{1}{2}\int d^3\boldsymbol{x}\,\Phi(\boldsymbol{x},t)\varrho(\boldsymbol{x},t)\\ &= q^2\sum_{ss'}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\frac{\Psi_s^+(\boldsymbol{x},t)\Psi_{s'}^+(\boldsymbol{x}',t)\Psi_{s'}(\boldsymbol{x}',t)\Psi_s(\boldsymbol{x},t)}{8\pi\epsilon_0|\boldsymbol{x}-\boldsymbol{x}'|},\end{aligned} \tag{21.67}$$

where the ordering of the field operators was performed to ensure correct expectation values for the interaction energy of 2-particle states after second quantization. The summation is over 4-spinor indices.

The resulting Hamiltonian in Coulomb gauge therefore has the form

$$\begin{aligned}H = &\int d^3\boldsymbol{x}\left(c\overline{\Psi}(\boldsymbol{x},t)\left[mc-\boldsymbol{\gamma}\cdot(\mathrm{i}\hbar\boldsymbol{\nabla}+q\boldsymbol{A}(\boldsymbol{x},t))\right]\Psi(\boldsymbol{x},t)\right.\\ &\left.+\frac{\epsilon_0}{2}\boldsymbol{E}_\perp^2(\boldsymbol{x},t)+\frac{1}{2\mu_0}\boldsymbol{B}^2(\boldsymbol{x},t)\right)\\ &+q^2\sum_{ss'}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\frac{\Psi_s^+(\boldsymbol{x},t)\Psi_{s'}^+(\boldsymbol{x}',t)\Psi_{s'}(\boldsymbol{x}',t)\Psi_s(\boldsymbol{x},t)}{8\pi\epsilon_0|\boldsymbol{x}-\boldsymbol{x}'|}.\end{aligned} \tag{21.68}$$

The momentum operator in Coulomb gauge follows from (21.63) and

$$\int d^3\boldsymbol{x}\,\epsilon_0\boldsymbol{E}_\parallel\times\boldsymbol{B} = -\int d^3\boldsymbol{x}\,\epsilon_0\Phi\Delta\boldsymbol{A} = \int d^3\boldsymbol{x}\,\varrho\boldsymbol{A} = q\int d^3\boldsymbol{x}\,\Psi^+\boldsymbol{A}\Psi$$

as

$$\boldsymbol{P} = \int d^3\boldsymbol{x}\left(\Psi^+\frac{\hbar}{\mathrm{i}}\boldsymbol{\nabla}\Psi+\epsilon_0\boldsymbol{E}_\perp\times\boldsymbol{B}\right). \tag{21.69}$$

All the representations (21.52), (21.62), (21.63) and (21.69) yield the same result in terms of $\boldsymbol{k}$ space operators for the momentum operator of the free Dirac field.

21.5 The non-relativistic limit of the Dirac equation

The Dirac basis (21.29) for the γ-matrices is convenient for the non-relativistic limit. Splitting off the time dependence due to the rest mass term

$$\Psi(\boldsymbol{x},t) = \begin{pmatrix} \psi(\boldsymbol{x},t) \\ \phi(\boldsymbol{x},t) \end{pmatrix} \exp\left(-\mathrm{i}\frac{mc^2}{\hbar}t\right)$$

in the Dirac equation (21.31) yields the equations

$$(\mathrm{i}\hbar\partial_t - q\Phi)\psi + c\underline{\boldsymbol{\sigma}}\cdot(\mathrm{i}\hbar\boldsymbol{\nabla} + q\boldsymbol{A})\phi = 0,$$

$$(\mathrm{i}\hbar\partial_t - q\Phi + 2mc^2)\phi + c\underline{\boldsymbol{\sigma}}\cdot(\mathrm{i}\hbar\boldsymbol{\nabla} + q\boldsymbol{A})\psi = 0.$$

This yields in the non-relativistic regime

$$\phi \simeq -\frac{1}{2mc}\underline{\boldsymbol{\sigma}}\cdot(\mathrm{i}\hbar\boldsymbol{\nabla} + q\boldsymbol{A})\psi \tag{21.70}$$

and substitution into the equation for ψ yields Pauli's equation[7]

$$\mathrm{i}\hbar\partial_t\psi = -\frac{1}{2m}(\hbar\boldsymbol{\nabla} - \mathrm{i}q\boldsymbol{A})^2\psi - \frac{q\hbar}{2m}\underline{\boldsymbol{\sigma}}\cdot\boldsymbol{B}\psi + q\Phi\psi. \tag{21.71}$$

The spin matrices for spin-1/2 Schrödinger fields are the upper block matrices in the spin matrices (21.54) for the full Dirac fields, $\underline{\boldsymbol{S}} = \hbar\underline{\boldsymbol{\sigma}}/2$, see also Section 8.1 and in particular equation (8.12).
If the external magnetic field $\boldsymbol{B}$ is approximately constant over the extension of the wave function $\psi(\boldsymbol{x},t)$ we can use

$$\boldsymbol{A}(\boldsymbol{x},t) = \frac{1}{2}\boldsymbol{B}(t)\times\boldsymbol{x}.$$

Substitution of the vector potential in equation (21.71) then yields the following linear terms in $\boldsymbol{B}$ in the Hamiltonian on the right hand side,

$$\begin{aligned}\mathrm{i}\frac{q\hbar}{2m}(\boldsymbol{B}\times\boldsymbol{x})\cdot\boldsymbol{\nabla} - \frac{q}{m}\boldsymbol{B}\cdot\underline{\boldsymbol{S}} &= -\frac{q}{2m}\boldsymbol{B}\cdot(\boldsymbol{M} + 2\underline{\boldsymbol{S}}) \\ &= -\frac{q}{e}\frac{\mu_B}{\hbar}\boldsymbol{B}\cdot(\boldsymbol{M} + 2\underline{\boldsymbol{S}}).\end{aligned} \tag{21.72}$$

Here $\mu_B = e\hbar/2m$ is the Bohr magneton, and we used the short hand notation $-\mathrm{i}\hbar\boldsymbol{x}\times\boldsymbol{\nabla} \to \boldsymbol{M}$ for the $\boldsymbol{x}$ representation of the angular momentum operator. Recall that this operator is actually given by

$$\boldsymbol{M} = \mathbf{x}\times\mathbf{p} = -\mathrm{i}\hbar\int d^3\boldsymbol{x}\,|\boldsymbol{x}\rangle\boldsymbol{x}\times\boldsymbol{\nabla}\langle\boldsymbol{x}|.$$

[7] W. Pauli, Z. Phys. 43, 601 (1927). Pauli actually only studied the time-independent Schrödinger equation with the Pauli term in the Hamiltonian, and although he mentions Schrödinger in the beginning, he seems to be more comfortable with Heisenberg's matrix mechanics in the paper.

Equation (21.72) shows that the Dirac equation also explains the double strength magnetic coupling of spin as compared to orbital angular momentum (often denoted as the *magneto-mechanical anomaly of the electron* or the *anomalous magnetic moment of the electron*). The corresponding electromagnetic currents in the non-relativistic regime are

$$\begin{aligned}\varrho &= q\psi^+\psi,\\ \boldsymbol{j} &= cq\left(\psi^+\underline{\boldsymbol{\sigma}}\phi + \phi^+\underline{\boldsymbol{\sigma}}\psi\right)\\ &= -\frac{q}{2m}\left(\psi^+\underline{\boldsymbol{\sigma}}\otimes\underline{\boldsymbol{\sigma}}\cdot(\mathrm{i}\hbar\boldsymbol{\nabla}+q\boldsymbol{A})\psi - (\mathrm{i}\hbar\boldsymbol{\nabla}\psi^+ - q\psi^+\boldsymbol{A})\cdot\underline{\boldsymbol{\sigma}}\otimes\underline{\boldsymbol{\sigma}}\psi\right),\end{aligned}$$

where $\underline{\boldsymbol{\sigma}}\otimes\underline{\boldsymbol{\sigma}}$ is the three-dimensional tensor with the (2×2)-matrix entries $\underline{\sigma}_i\cdot\underline{\sigma}_j$ (we can think of it as a (3×3)-matrix containing (2×2)-matrices as entries). Substitution of

$$\underline{\boldsymbol{\sigma}}\otimes\underline{\boldsymbol{\sigma}} = \underline{1} + \mathrm{i}\boldsymbol{e}_i\otimes\boldsymbol{e}_j\varepsilon_{ijk}\underline{\sigma}_k$$

yields

$$\boldsymbol{j} = \frac{q}{2\mathrm{i}m}\left(\psi^+\cdot\hbar\boldsymbol{\nabla}\psi - \hbar\boldsymbol{\nabla}\psi^+\cdot\psi - 2\mathrm{i}q\psi^+\boldsymbol{A}\psi\right) + \frac{q\hbar}{2m}\boldsymbol{\nabla}\times\left(\psi^+\underline{\boldsymbol{\sigma}}\psi\right). \tag{21.73}$$

The corresponding non-relativistics approximations for the Lagrange density $\mathcal{L}$, the energy density $\mathcal{H}$ and the momentum density $\boldsymbol{\mathcal{P}}$ are

$$\begin{aligned}\mathcal{L} &= \frac{\mathrm{i}\hbar}{2}\left(\psi^+\cdot\frac{\partial}{\partial t}\psi - \frac{\partial}{\partial t}\psi^+\cdot\psi\right) - q\psi^+\Phi\psi + \frac{q\hbar}{2m}\psi^+\underline{\boldsymbol{\sigma}}\cdot\boldsymbol{B}\psi\\ &\quad + \frac{1}{2m}(\mathrm{i}\hbar\boldsymbol{\nabla}\psi^+ - q\psi^+\boldsymbol{A})\cdot(\mathrm{i}\hbar\boldsymbol{\nabla}\psi + q\boldsymbol{A}\psi) - \frac{1}{4\mu_0}F_{\mu\nu}F^{\mu\nu},\end{aligned} \tag{21.74}$$

$$\begin{aligned}\mathcal{H} &= \frac{1}{2m}(\hbar\boldsymbol{\nabla}\psi^+ + \mathrm{i}q\psi^+\boldsymbol{A})\cdot(\hbar\boldsymbol{\nabla}\psi - \mathrm{i}q\boldsymbol{A}\psi) - \frac{q\hbar}{2m}\psi^+\underline{\boldsymbol{\sigma}}\cdot\boldsymbol{B}\psi\\ &\quad + \frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2,\end{aligned} \tag{21.75}$$

$$\boldsymbol{\mathcal{P}} = \frac{\hbar}{2\mathrm{i}}\left(\psi^+\cdot\boldsymbol{\nabla}\psi - \boldsymbol{\nabla}\psi^+\cdot\psi\right) - q\psi^+\boldsymbol{A}\psi + \epsilon_0\boldsymbol{E}\times\boldsymbol{B}. \tag{21.76}$$

The Hamiltonian and momentum operators in Coulomb gauge are

$$\begin{aligned}H &= \int d^3\boldsymbol{x}\left(-\frac{1}{2m}\psi^+(\boldsymbol{x},t)[\hbar\boldsymbol{\nabla} - \mathrm{i}q\boldsymbol{A}(\boldsymbol{x},t)]^2\psi(\boldsymbol{x},t)\right.\\ &\quad \left. + \frac{\epsilon_0}{2}\boldsymbol{E}_\perp^2(\boldsymbol{x},t) + \frac{1}{2\mu_0}\boldsymbol{B}^2(\boldsymbol{x},t) - \frac{q\hbar}{2m}\psi^+(\boldsymbol{x},t)\underline{\boldsymbol{\sigma}}\cdot\boldsymbol{B}(\boldsymbol{x},t)\psi(\boldsymbol{x},t)\right)\\ &\quad + q^2\sum_{ss'=1}^{2}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\frac{\psi_s^+(\boldsymbol{x},t)\psi_{s'}^+(\boldsymbol{x}',t)\psi_{s'}(\boldsymbol{x}',t)\psi_s(\boldsymbol{x},t)}{8\pi\epsilon_0|\boldsymbol{x}-\boldsymbol{x}'|}.\end{aligned} \tag{21.77}$$

and (cf. equation (21.69)

$$\boldsymbol{P} = \int d^3\boldsymbol{x}\left(\psi^+\frac{\hbar}{\mathrm{i}}\boldsymbol{\nabla}\psi + \epsilon_0\boldsymbol{E}_\perp\times\boldsymbol{B}\right). \tag{21.78}$$

It is interesting to note that if we write the current density (21.73) as

$$\boldsymbol{j} = \boldsymbol{J} + \frac{q\hbar}{2m}\boldsymbol{\nabla} \times \left(\psi^+ \underline{\boldsymbol{\sigma}} \psi\right) = \boldsymbol{J} + \frac{q}{e}\mu_B \boldsymbol{\nabla} \times \left(\psi^+ \underline{\boldsymbol{\sigma}} \psi\right)$$

we can write Ampère's law with Maxwell's correction term as

$$\boldsymbol{\nabla} \times \left(\boldsymbol{B} - \frac{q}{e}\mu_0 \mu_B \psi^+ \underline{\boldsymbol{\sigma}} \psi\right) = \boldsymbol{\nabla} \times \boldsymbol{B}_{class} = \mu_0 \boldsymbol{J} + \mu_0 \epsilon_0 \frac{\partial}{\partial t}\boldsymbol{E},$$

i.e. the "spin density"

$$\boldsymbol{S}(\boldsymbol{x}, t) = \frac{\hbar}{2}\psi^+(\boldsymbol{x}, t)\underline{\boldsymbol{\sigma}}\psi(\boldsymbol{x}, t)$$

adds a spin magnetic field to the magnetic field $\boldsymbol{B}_{class}$ which is generated by orbital currents $\boldsymbol{J}$ and time-dependent electric fields $\boldsymbol{E}$,

$$\boldsymbol{B}(\boldsymbol{x}, t) = \boldsymbol{B}_{class}(\boldsymbol{x}, t) + \frac{2q}{e\hbar}\mu_0 \mu_B \boldsymbol{S}(\boldsymbol{x}, t) = \boldsymbol{B}_{class}(\boldsymbol{x}, t) + \mu_0 \frac{q}{m}\boldsymbol{S}(\boldsymbol{x}, t).$$

21.6 Two-particle scattering cross sections

We have discussed cross sections with one free particle in the initial or final states of a scattering event in the framework of potential scattering theory in Chapters 11 and 13, or in photon emission, absorption or scattering off bound electrons in Sections 18.5-18.8. The techniques that we have discussed so far cover many applications of scattering theory in materials science and condensed matter physics, but eventually we also wish to understand electron-electron scattering, electron-photon scattering, or electron-phonon scattering if the electrons are free or quasi-free conduction electrons in metals or semiconductors. In these cases we are discussing scattering events with two particles in the initial or final states, if we do not want to rely on semi-classical potential approximations for the photons or phonons. We should therefore address the question how to generalize the equations from Sections 13.6 and 18.8, which dealt with the case of one free particle in the initial and final state.
Let us recall from Section 13.6 that with a free particle with wave vectors $\boldsymbol{k}$ and $\boldsymbol{k}'$ in the initial and final state, the scattering matrix element for a monochromatic perturbation $W(t) \sim \exp(-\mathrm{i}\omega t)$

$$S_{\boldsymbol{k}',\boldsymbol{k}} = \langle \boldsymbol{k}' | U_D(\infty, -\infty) | \boldsymbol{k} \rangle = -\mathrm{i}\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}\delta(\omega(k') - \omega(k) - \omega)$$

has dimension length^3 due to the length dimensions of the external states, and yields a differential scattering cross section

$$d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} = d^3\boldsymbol{k}' \frac{|S_{\boldsymbol{k}',\boldsymbol{k}}|^2}{T dj(\boldsymbol{k})/d^3\boldsymbol{k}} = d^3\boldsymbol{k}' \frac{|\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}|^2}{2\pi dj(\boldsymbol{k})/d^3\boldsymbol{k}}\delta(\omega(k') - \omega(k) - \omega).$$

Here we substituted the more precise notation $dj(\boldsymbol{k})/d^3\boldsymbol{k}$ for the incoming current density j_{in} per unit of $\boldsymbol{k}$ space volume. Substitution of the current density for a free particle of momentum $\hbar\boldsymbol{k}$

$$\frac{d\boldsymbol{j}(\boldsymbol{k})}{d^3\boldsymbol{k}} = \frac{\boldsymbol{v}}{(2\pi)^3}$$

yields

$$v d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} = 4\pi^2 \left|\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}\right|^2 \delta(\omega(k') - \omega(k) - \omega) d^3\boldsymbol{k}', \tag{21.79}$$

see also equation (18.74), where we found this equation for photon scattering off atoms or molecules.

Now suppose that we have two free particles with momenta $\boldsymbol{k}$ and $\boldsymbol{q}$ in the initial state, and they scatter into free particles with momenta $\boldsymbol{k}'$ and $\boldsymbol{q}'$ in the final state. We also assume that the scattering preserves total energy and momentum. The corresponding scattering matrix element

$$S_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}} = \langle \boldsymbol{k}', \boldsymbol{q}' | U_D(\infty, -\infty) | \boldsymbol{k}, \boldsymbol{q} \rangle = -\mathrm{i}\mathcal{M}_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}} \delta(k' + q' - k - q) \tag{21.80}$$

has dimension length^6. This is consistent with the fact that $|S_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}}|^2$ is a transition probability density per volume units $d^3\boldsymbol{k}' d^3\boldsymbol{q}' d^3\boldsymbol{k} d^3\boldsymbol{q}$ in wave vector space.

For ease of the present discussion, we also assume that the scattering particles are different, like in electron-photon or electron-phonon scattering, and we will use markers e and γ to label quantities refering to the different particles. The notation is motivated from electron-photon scattering, but we will develop the formalism in this section with general pairs of particles of masses m_e and m_γ in mind.

Suppose the two particles have momentum 4-vectors

$$p_e = \hbar k = \hbar(\omega_e/c, \boldsymbol{k}), \quad p_\gamma = \hbar q = \hbar(\omega_\gamma/c, \boldsymbol{q})$$

relative to the laboratory frame in which we observe the collisions. The scattering rate will be proportional to the product

$$\frac{d\varrho_e(\boldsymbol{k})}{d^3\boldsymbol{k}} \frac{dj_\gamma(\boldsymbol{q})}{d^3\boldsymbol{q}} = \frac{d\varrho_e(\boldsymbol{k})}{d^3\boldsymbol{k}} \frac{d\varrho_\gamma(\boldsymbol{q})}{d^3\boldsymbol{q}} \tilde{v}_{e\gamma},$$

where

$$\tilde{v}_{e\gamma} = c^2 \left| \frac{\boldsymbol{k}}{\omega_e} - \frac{\boldsymbol{q}}{\omega_\gamma} \right| \tag{21.81}$$

is the relative speed between the two particles that *we* assign from the point of view of our laboratory frame. The speed $\tilde{v}_{e\gamma}$ is usually replaced with another measure for relative speed between the two particles,

$$v_{e\gamma} = \frac{c^3}{\omega_e \omega_\gamma} \sqrt{(k \cdot q)^2 - \frac{m_e^2 m_\gamma^2 c^4}{\hbar^4}}, \tag{21.82}$$

which agrees with $\tilde{v}_{e\gamma}$ in laboratory frames in which the two momentum vectors $\boldsymbol{p}_e$ and $\boldsymbol{p}_\gamma$ are parallel or anti-parallel, or where the laboratory frame coincides with the rest frame of one of the two particles:

$$\tilde{v}_{e\gamma}^2 - v_{e\gamma}^2 = \frac{c^6}{\omega_e^2\omega_\gamma^2}\,|\boldsymbol{k}|^2\,|\boldsymbol{q}|^2\,\big(1-\cos^2\vartheta\big).$$

Here ϑ is the angle between $\boldsymbol{p}_e$ and $\boldsymbol{p}_\gamma$. E.g. in the rest frame of the e-particle, $\hbar k_e = \hbar(\omega_e/c, \boldsymbol{0}) = (m_e c, \boldsymbol{0})$, we find

$$v_{e\gamma} = \frac{c}{\omega_\gamma}\sqrt{\omega_\gamma^2 - \frac{m_\gamma^2 c^4}{\hbar^2}} = c^2\frac{|\boldsymbol{p}_\gamma|}{E_\gamma} = v_\gamma,$$

and in the center of mass frame of the two particles, $\boldsymbol{k} = -\boldsymbol{q}$, we also find the difference of particle velocities,

$$\begin{aligned} v_{e\gamma}^2 &= c^2\frac{\hbar^4(\omega_e\omega_\gamma + c^2\boldsymbol{k}^2)^2 - m_e^2 m_\gamma^2 c^8}{\hbar^4\omega_e^2\omega_\gamma^2} \\ &= c^4\frac{2\hbar^2 c^2\boldsymbol{k}^4 + 2\hbar^2\omega_e\omega_\gamma\boldsymbol{k}^2 + c^4\boldsymbol{k}^2(m_e^2+m_\gamma^2)}{\hbar^2\omega_e^2\omega_\gamma^2} = c^4\boldsymbol{k}^2\frac{\omega_e^2+\omega_\gamma^2+2\omega_e\omega_\gamma}{\omega_e^2\omega_\gamma^2} \\ &= \left(c^2\frac{\boldsymbol{k}}{\omega_e} - c^2\frac{\boldsymbol{q}}{\omega_\gamma}\right)^2. \end{aligned} \tag{21.83}$$

As a byproduct we also find another useful formula for the relative speed in the center of mass frame,

$$v_{e\gamma} = c^2|\boldsymbol{k}|\frac{\omega_e+\omega_\gamma}{\omega_e\omega_\gamma}. \tag{21.84}$$

Please keep in mind that (21.84) is the relative particle speed assigned to the two colliding particles by an observer at rest in the center of mass frame, but not the speed of one particle relative to the other particle as measured in the rest frame of one of the particles.
The differential cross section for two-particle scattering can then be defined through the equation

$$\begin{aligned} v d\sigma_{\boldsymbol{k},\boldsymbol{q}\to\boldsymbol{k}',\boldsymbol{q}'} &= v d^3\boldsymbol{k}' d^3\boldsymbol{q}'\frac{|S_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}}|^2}{VT(d\varrho_e/d^3\boldsymbol{k})(dj_\gamma/d^3\boldsymbol{q})} \\ &= d^3\boldsymbol{k}' d^3\boldsymbol{q}'\frac{|S_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}}|^2}{VT(d\varrho_e/d^3\boldsymbol{k})(d\varrho_\gamma/d^3\boldsymbol{q})}. \end{aligned} \tag{21.85}$$

In words, we divide the scattering rate $d^3\boldsymbol{k}' d^3\boldsymbol{q}'\,|S_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}}|^2\,d^3\boldsymbol{k} d^3\boldsymbol{q}/T$ between wave vector volumes $d^3\boldsymbol{k} d^3\boldsymbol{q} \to d^3\boldsymbol{k}' d^3\boldsymbol{q}'$ by the number of scattering centers $V d\varrho_e$ in the phase space volume $V d^3\boldsymbol{k}$ and the incoming particle flux dj_γ in the wave vector volume $d^3\boldsymbol{q}$ to calculate $d\sigma_{\boldsymbol{k},\boldsymbol{q}\to\boldsymbol{k}',\boldsymbol{q}'}$.

If we substitute the scattering amplitude $\mathcal{M}_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}}$ for the scattering matrix element and use for the 4-dimensional δ function in momentum space the equation

$$\delta^4(0) = \lim_{k\to 0} \frac{1}{(2\pi)^4} \int d^4x \, \exp(\mathrm{i}k \cdot x) = \frac{cVT}{(2\pi)^4},$$

we find

$$v d\sigma_{\boldsymbol{k},\boldsymbol{q}\to\boldsymbol{k}',\boldsymbol{q}'} = d^3\boldsymbol{k}' d^3\boldsymbol{q}' \frac{c\,|\mathcal{M}_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}}|^2}{(2\pi)^4 (d\varrho_e/d^3\boldsymbol{k})(d\varrho_\gamma/d^3\boldsymbol{q})} \delta^4(k' + q' - k - q). \quad (21.86)$$

The density per $\boldsymbol{x}$ space volume and per unit $d^3\boldsymbol{k}$ of $\boldsymbol{k}$ space volume for momentum eigenstates is

$$\frac{d\varrho}{d^3\boldsymbol{k}} = \frac{1}{(2\pi)^3}.$$

This yields

$$v d\sigma_{\boldsymbol{k},\boldsymbol{q}\to\boldsymbol{k}',\boldsymbol{q}'} = 4\pi^2 c\,|\mathcal{M}_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}}|^2\, \delta^4(k' + q' - k - q) d^3\boldsymbol{k}' d^3\boldsymbol{q}'. \quad (21.87)$$

Note from equation (21.80) that the two-particle scattering amplitude $\mathcal{M}_{\boldsymbol{k}',\boldsymbol{q}';\boldsymbol{k},\boldsymbol{q}}$ has the dimension length^2 while the single-particle scattering amplitude $\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}}$ has dimension length^3/time due to the use of a δ function in frequencies rather than wave numbers in the single-particle case.

We can derive a single-particle scattering cross section from (21.87) by integrating over the final wave number of one of the two particles, e.g. $\boldsymbol{q}'$, while considering its initial wave number fixed, e.g. $\boldsymbol{q} = \boldsymbol{0}$. This yields

$$\begin{aligned} v d\sigma_{\boldsymbol{k}\to\boldsymbol{k}'} &= v \int d^3\boldsymbol{q}' \frac{d\sigma_{\boldsymbol{k},\boldsymbol{0}\to\boldsymbol{k}',\boldsymbol{q}'}}{d^3\boldsymbol{q}'} \\ &= 4\pi^2 c^2\, |\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}-\boldsymbol{k}';\boldsymbol{k},\boldsymbol{0}}|^2\, \delta(\omega(\boldsymbol{k}') - \omega(\boldsymbol{k}) - \omega_q) d^3\boldsymbol{k}', \end{aligned}$$

with

$$\omega_q = \omega(\boldsymbol{q} = \boldsymbol{0}) - \omega(\boldsymbol{q}' = \boldsymbol{k} - \boldsymbol{k}')$$

and a resulting single particle scattering amplitude $\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}} = c\mathcal{M}_{\boldsymbol{k}',\boldsymbol{k}-\boldsymbol{k}';\boldsymbol{k},\boldsymbol{0}}$.

Measures for final states with two identical particles

To explain the necessary modifications of the previous results if we have two identical particles in the final state, we first consider decay of a normalizable state $|i\rangle$ into two identical particles with momenta $\hbar\boldsymbol{k}_1$ and $\hbar\boldsymbol{k}_2$.

The initial state belongs to a set of orthonormal states, $\langle i|j\rangle = \delta_{ij}$. For the final states with two identical particles, we have to take into account that the decomposition of unity on identical 2-particle states is

$$\begin{aligned} 1_{\text{identical 2-particle states}} &= \frac{1}{2} \int d^3\boldsymbol{k}_1 \int d^3\boldsymbol{k}_2\, |\boldsymbol{k}_1, \boldsymbol{k}_2\rangle \langle \boldsymbol{k}_1, \boldsymbol{k}_2| \\ &= \frac{1}{2} \int d^3\boldsymbol{k}_1 \int d^3\boldsymbol{k}_2\, a^+(\boldsymbol{k}_1) a^+(\boldsymbol{k}_2) |0\rangle \langle 0| a(\boldsymbol{k}_2) a(\boldsymbol{k}_1). \end{aligned}$$

If the scattering matrix allows only for decay into the two-particle states, unitarity $U_D^+ U_D = 1$ (or equivalently $S^+ S = 1$) implies

$$\frac{1}{2}\int d^3\boldsymbol{k}_1 \int d^3\boldsymbol{k}_2 \; |\langle \boldsymbol{k}_1, \boldsymbol{k}_2 | U_D(\infty, -\infty)|i\rangle|^2 = 1.$$

The proper probability density for the transition $|i\rangle \to |\boldsymbol{k}_1, \boldsymbol{k}_2\rangle$ is therefore

$$w_{i\to \boldsymbol{k}_1,\boldsymbol{k}_2} = \frac{1}{2} d^3\boldsymbol{k}_1 d^3\boldsymbol{k}_2 \; |\langle \boldsymbol{k}_1, \boldsymbol{k}_2 | U_D(\infty, -\infty)|i\rangle|^2 .$$

Equation (21.87) for the two-particle scattering cross section must therefore be modified if the final state contains two identical particles,

$$\begin{aligned} v d\sigma_{\boldsymbol{k}_1,\boldsymbol{k}_2\to \boldsymbol{k}_1',\boldsymbol{k}_2'} &= 4\pi^2 c \left|\mathcal{M}_{\boldsymbol{k}_1',\boldsymbol{k}_2';\boldsymbol{k}_1,\boldsymbol{k}_2}\right|^2 \delta^4(k_1' + k_2' - k_1 - k_2) \\ &\quad \times \frac{1}{2} d^3\boldsymbol{k}_1' d^3\boldsymbol{k}_2', \end{aligned} \tag{21.88}$$

and the total two-particle cross section is

$$\begin{aligned} \sigma &= \int d^3\boldsymbol{k}_1' \int d^3\boldsymbol{k}_2' \, \frac{d\sigma_{\boldsymbol{k}_1,\boldsymbol{k}_2\to \boldsymbol{k}_1',\boldsymbol{k}_2'}}{d^3\boldsymbol{k}_1' d^3\boldsymbol{k}_2'} \\ &= \frac{1}{2}\int d^3\boldsymbol{k}_1' \int d^3\boldsymbol{k}_2' \, 4\pi^2 \frac{c}{v} \left|\mathcal{M}_{\boldsymbol{k}_1',\boldsymbol{k}_2';\boldsymbol{k}_1,\boldsymbol{k}_2}\right|^2 \delta^4(k_1' + k_2' - k_1 - k_2). \end{aligned} \tag{21.89}$$

However, if we want to derive an effective *single-particle* differential scattering cross section $d\sigma/d\Omega$ from $d\sigma_{\boldsymbol{k}_1,\boldsymbol{k}_2\to \boldsymbol{k}_1',\boldsymbol{k}_2'}$ by integrating over the momentum of one particle and the magnitude of momentum of the second particle using the energy-momentum conserving δ function, we have to take into account that the particle observed in direction $d\Omega$ can be either one of the two scattered particles:

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= \int d^3\boldsymbol{k}_1' \int_0^\infty d|\boldsymbol{k}_2'| \, |\boldsymbol{k}_2'|^2 \frac{d\sigma_{\boldsymbol{k}_1,\boldsymbol{k}_2\to \boldsymbol{k}_1',\boldsymbol{k}_2'}}{d^3\boldsymbol{k}_1' d^3\boldsymbol{k}_2'} \\ &\quad + \int d^3\boldsymbol{k}_2' \int_0^\infty d|\boldsymbol{k}_1'| \, |\boldsymbol{k}_1'|^2 \frac{d\sigma_{\boldsymbol{k}_1,\boldsymbol{k}_2\to \boldsymbol{k}_1',\boldsymbol{k}_2'}}{d^3\boldsymbol{k}_1' d^3\boldsymbol{k}_2'}. \end{aligned}$$

In the center of mass frame this reduces to a factor of 2,

$$\frac{d\sigma}{d\Omega} = 2\int d^3\boldsymbol{k}_2' \int_0^\infty d|\boldsymbol{k}_1'| \, |\boldsymbol{k}_1'|^2 \frac{d\sigma_{\boldsymbol{k}_1,\boldsymbol{k}_2\to \boldsymbol{k}_1',\boldsymbol{k}_2'}}{d^3\boldsymbol{k}_1' d^3\boldsymbol{k}_2'}. \tag{21.90}$$

If we then wish to calculate the total two-particle scattering cross section (21.89) from the single-particle differential cross section (21.90), we have to compensate with a factor 1/2,

$$\sigma = \frac{1}{2}\int d\Omega \, \frac{d\sigma}{d\Omega}. \tag{21.91}$$

In practice one is often only interested in the effective single-particle differential cross section (21.90) and the total two-particle scattering cross section σ.

The factor 1/2 is then usually neglected in the differential two-particle cross section $d\sigma_{\boldsymbol{k}_1,\boldsymbol{k}_2\to\boldsymbol{k}_1',\boldsymbol{k}_2'}/(d^3\boldsymbol{k}_1' d^3\boldsymbol{k}_2')$, so that the factor of 2 is not needed in the calculation of $d\sigma/d\Omega$ (21.90) because it has been absorbed in $d\sigma_{\boldsymbol{k}_1,\boldsymbol{k}_2\to\boldsymbol{k}_1',\boldsymbol{k}_2'}/(d^3\boldsymbol{k}_1' d^3\boldsymbol{k}_2')$. However, the factor 1/2 is still needed in the calculation of the total two-particle cross section σ from $d\sigma/d\Omega$ according to equation (21.91).

21.7 Photon scattering by free electrons

Photon scattering by free or quasi-free electrons is also known as Compton scattering. The cross section for this process had been calculated in leading order by Klein and Nishina[8].
The electron-photon interaction term from (21.68) is

$$\mathcal{H}_{e\gamma} = ec\overline{\Psi}\boldsymbol{\gamma}\cdot\boldsymbol{A}\Psi. \tag{21.92}$$

We denote the wave vectors of the incoming photon and electron with $\boldsymbol{q}$ and $\boldsymbol{k}$, respectively. The relevant second order matrix element for scattering of photons by free electrons is

$$\begin{aligned}
S_{fi} &= S_{\boldsymbol{k}',s';\boldsymbol{q}',\alpha'|\boldsymbol{k},s;\boldsymbol{q},\alpha} \\
&= -\frac{e^2c^2}{\hbar^2}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt'\,\langle\boldsymbol{k}',s';\boldsymbol{q}',\alpha'|\exp\left(\frac{\mathrm{i}}{\hbar}H_0 t\right) \\
&\quad\times\overline{\Psi}(\boldsymbol{x})\boldsymbol{\gamma}\cdot\boldsymbol{A}(\boldsymbol{x})\Psi(\boldsymbol{x})\exp\left(-\frac{\mathrm{i}}{\hbar}H_0(t-t')\right)\overline{\Psi}(\boldsymbol{x}')\boldsymbol{\gamma}\cdot\boldsymbol{A}(\boldsymbol{x}')\Psi(\boldsymbol{x}') \\
&\quad\times\exp\left(-\frac{\mathrm{i}}{\hbar}H_0 t'\right)|\boldsymbol{k},s;\boldsymbol{q},\alpha\rangle \\
&= -\frac{e^2}{\hbar^2}\int d^4x\int d^4x'\,\Theta(t-t')\langle\boldsymbol{k}',s';\boldsymbol{q}',\alpha'|\overline{\Psi}(x)\boldsymbol{\gamma}\cdot\boldsymbol{A}(x)\Psi(x) \\
&\quad\times\overline{\Psi}(x')\boldsymbol{\gamma}\cdot\boldsymbol{A}(x')\Psi(x')|\boldsymbol{k},s;\boldsymbol{q},\alpha\rangle.
\end{aligned}$$

Here $\boldsymbol{A}(x)\equiv\boldsymbol{A}_D(\boldsymbol{x},t)$ and $\Psi(x)\equiv\Psi_D(\boldsymbol{x},t)$ are the freely evolving field operators (18.20,21.49) in the interaction picture.
We can insert a decomposition of unity between the two vertex operators $\overline{\Psi}\boldsymbol{\gamma}\cdot\boldsymbol{A}\Psi$ with a fermionic and a photon factor,

$$1 = 1_f\otimes 1_\gamma.$$

The relevant parts in the photon factor have zero or two intermediate photons,

$$1_\gamma \Rightarrow |0\rangle\langle 0| + \frac{1}{2}\sum_{\beta,\beta'}\int d^3\boldsymbol{K}\int d^3\boldsymbol{K}'\,|\boldsymbol{K},\beta;\boldsymbol{K}',\beta'\rangle\langle\boldsymbol{K},\beta;\boldsymbol{K}',\beta'|,$$

[8] O. Klein, Y. Nishina, Z. Phys. 52, 853 (1929).

while for the intermediate fermion states only states with one intermediate electron or with two intermediate electrons and a positron contribute,

$$
\begin{aligned}
1_f \Rightarrow & \sum_\sigma \int d^3\boldsymbol{\kappa}\, b_\sigma^+(\boldsymbol{\kappa})|0\rangle\langle 0|b_\sigma(\boldsymbol{\kappa}) \\
& + \frac{1}{2}\sum_{\sigma,\sigma',\nu}\int d^3\boldsymbol{\kappa}\int d^3\boldsymbol{\kappa}'\int d^3\boldsymbol{\lambda}\, b_\sigma^+(\boldsymbol{\kappa}) b_{\sigma'}^+(\boldsymbol{\kappa}') d_\nu^+(\boldsymbol{\lambda})|0\rangle \\
& \times\langle 0|d_\nu(\boldsymbol{\lambda}) b_{\sigma'}(\boldsymbol{\kappa}') b_\sigma(\boldsymbol{\kappa}).
\end{aligned}
$$

The full photon matrix element is

$$
\begin{aligned}
&\langle \boldsymbol{q}', \alpha'|\boldsymbol{A}(x)\otimes\boldsymbol{A}(x')|\boldsymbol{q},\alpha\rangle = \frac{\hbar\mu_0 c}{16\pi^3\sqrt{|\boldsymbol{q}||\boldsymbol{q}'|}}\Big(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\otimes\boldsymbol{\epsilon}_\alpha(\boldsymbol{q}) \\
&\times\exp[\mathrm{i}(q\cdot x' - q'\cdot x)] + \boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\otimes\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\exp[\mathrm{i}(q\cdot x - q'\cdot x')]\Big),
\end{aligned}
$$

where the first term arises from the term without intermediate photons and the second term arises from the term with two intermediate photons after integrating the intermediate photon momenta $\boldsymbol{K}$ and $\boldsymbol{K}'$.
Evaluation of the fermion matrix element with an electron in the intermediate state yields

$$
\begin{aligned}
&\sum_\sigma \langle \boldsymbol{k}', s'|\overline{\Psi}(x)\boldsymbol{\gamma}\Psi(x) b_\sigma^+(\boldsymbol{\kappa})|0\rangle\otimes\langle 0|b_\sigma(\boldsymbol{\kappa})\overline{\Psi}(x')\boldsymbol{\gamma}\Psi(x')|\boldsymbol{k},s\rangle \\
&= \sum_\sigma \frac{\exp[\mathrm{i}\kappa\cdot(x-x') - \mathrm{i}k'\cdot x + \mathrm{i}k\cdot x']}{(2\pi)^6 4E(\boldsymbol{\kappa})\sqrt{E(\boldsymbol{k}')E(\boldsymbol{k})}}\overline{u}_{s'}(\boldsymbol{k}')\boldsymbol{\gamma}u_\sigma(\boldsymbol{\kappa})\otimes\overline{u}_\sigma(\boldsymbol{\kappa})\boldsymbol{\gamma}u_s(\boldsymbol{k}).
\end{aligned}
$$

We can subsitute the sum over intermediate u spinors using equation (21.45),

$$
\begin{aligned}
&\sum_\sigma \langle \boldsymbol{k}', s'|\overline{\Psi}(x)\boldsymbol{\gamma}\Psi(x) b_\sigma^+(\boldsymbol{\kappa})|0\rangle\otimes\langle 0|b_\sigma(\boldsymbol{\kappa})\overline{\Psi}(x')\boldsymbol{\gamma}\Psi(x')|\boldsymbol{k},s\rangle \\
&= \frac{\exp[\mathrm{i}\kappa\cdot(x-x') - \mathrm{i}k'\cdot x + \mathrm{i}k\cdot x']}{(2\pi)^6 4E(\boldsymbol{\kappa})\sqrt{E(\boldsymbol{k}')E(\boldsymbol{k})}}\boldsymbol{e}_i\otimes\boldsymbol{e}_j \\
&\quad\times\overline{u}_{s'}(\boldsymbol{k}')\gamma^i\left(mc^2 - \hbar c\boldsymbol{\gamma}\cdot\boldsymbol{\kappa} - \gamma^0 E(\boldsymbol{\kappa})\right)\gamma^j u_s(\boldsymbol{k}).
\end{aligned}
$$

Assembling the pieces so far then yields the amplitude with a single intermediate fermion,

$$
\begin{aligned}
S_{fi}^{(1)} = & -\int\frac{d^3\boldsymbol{\kappa}}{E(\boldsymbol{\kappa})}\int d^4x\int d^4x'\,\frac{e^2\Theta(t-t')}{8(2\pi)^9\epsilon_0\hbar c\sqrt{|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k})E(\boldsymbol{k}')}} \\
& \times\overline{u}_{s'}(\boldsymbol{k}')\Big[\left(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma}\right)\left(mc^2 - \hbar c\boldsymbol{\kappa}\cdot\boldsymbol{\gamma} - \gamma^0 E(\boldsymbol{\kappa})\right)\left(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma}\right) \\
& \times\exp\left[\mathrm{i}(\kappa - k' - q')\cdot x + \mathrm{i}(k + q - \kappa)\cdot x'\right] \\
& + \left(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma}\right)\left(mc^2 - \hbar c\boldsymbol{\kappa}\cdot\boldsymbol{\gamma} - \gamma^0 E(\boldsymbol{\kappa})\right)\left(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma}\right) \\
& \times\exp\left[\mathrm{i}(\kappa - k' + q)\cdot x + \mathrm{i}(k - q' - \kappa)\cdot x'\right]\Big]u_s(\boldsymbol{k}).
\end{aligned}
\tag{21.93}
$$

The fermion matrix element with three intermediate fermions is

$$\frac{1}{2}\sum_{\sigma,\sigma',\nu}\langle \boldsymbol{k}', s'|\overline{\Psi}(x)\boldsymbol{\gamma}\Psi(x)b^+_\sigma(\boldsymbol{\kappa})b^+_{\sigma'}(\boldsymbol{\kappa}')d^+_\nu(\boldsymbol{\lambda})|0\rangle$$
$$\otimes\langle 0|d_\nu(\boldsymbol{\lambda})b_{\sigma'}(\boldsymbol{\kappa}')b_\sigma(\boldsymbol{\kappa})\overline{\Psi}(x')\boldsymbol{\gamma}\Psi(x')|\boldsymbol{k}, s\rangle$$
$$= -\sum_\nu \delta(\boldsymbol{\kappa}'-\boldsymbol{k}')\delta(\boldsymbol{\kappa}-\boldsymbol{k})\frac{\exp[\mathrm{i}\lambda\cdot(x-x')+\mathrm{i}k\cdot x-\mathrm{i}k'\cdot x']}{(2\pi)^6 4E(\boldsymbol{\lambda})\sqrt{E(\boldsymbol{k}')E(\boldsymbol{k})}}$$
$$\times\overline{v}_\nu(\boldsymbol{\lambda})\boldsymbol{\gamma}u_s(\boldsymbol{k})\otimes\overline{u}_{s'}(\boldsymbol{k}')\boldsymbol{\gamma}v_\nu(\boldsymbol{\lambda}).$$

The last line has been simplified from an expression which is symmetric in the intermediate momenta $\boldsymbol{\kappa}$ and $\boldsymbol{\kappa}'$ by taking into account that those momenta will be integrated.
We can subsitute the sum over intermediate v spinors using equation (21.47),

$$\frac{1}{2}\sum_{\sigma,\sigma',\nu}\langle \boldsymbol{k}', s'|\overline{\Psi}(x)\boldsymbol{\gamma}\Psi(x)b^+_\sigma(\boldsymbol{\kappa})b^+_{\sigma'}(\boldsymbol{\kappa}')d^+_\nu(\boldsymbol{\lambda})|0\rangle$$
$$\otimes\langle 0|d_\nu(\boldsymbol{\lambda})b_{\sigma'}(\boldsymbol{\kappa}')b_\sigma(\boldsymbol{\kappa})\overline{\Psi}(x')\boldsymbol{\gamma}\Psi(x')|\boldsymbol{k}, s\rangle$$
$$= \delta(\boldsymbol{\kappa}'-\boldsymbol{k}')\delta(\boldsymbol{\kappa}-\boldsymbol{k})\frac{\exp[\mathrm{i}\lambda\cdot(x-x')+\mathrm{i}k\cdot x-\mathrm{i}k'\cdot x']}{(2\pi)^6 4E(\boldsymbol{\lambda})\sqrt{E(\boldsymbol{k}')E(\boldsymbol{k})}}$$
$$\times\boldsymbol{e}_i\otimes\boldsymbol{e}_j\overline{u}_{s'}(\boldsymbol{k}')\gamma^j\left(mc^2+\hbar c\boldsymbol{\gamma}\cdot\boldsymbol{\lambda}+\gamma^0E(\boldsymbol{\lambda})\right)\gamma^i u_s(\boldsymbol{k}).$$

If we substitute $\boldsymbol{\lambda}\to\boldsymbol{\kappa}$ (after integration over the intermediate electron momenta) for the wave vector of the intermediate positron, the contribution from three intermediate fermions to the scattering matrix element is

$$\begin{aligned}S^{(3)}_{fi} = -\int\frac{d^3\boldsymbol{\kappa}}{E(\boldsymbol{\kappa})}\int d^4x\int d^4x'\,\frac{e^2\Theta(t-t')}{8(2\pi)^9\epsilon_0\hbar c\sqrt{|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k})E(\boldsymbol{k}')}}\\ \times\overline{u}_{s'}(\boldsymbol{k}')\Big[\left(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma}\right)\left(mc^2+\hbar c\boldsymbol{\kappa}\cdot\boldsymbol{\gamma}+\gamma^0E(\boldsymbol{\kappa})\right)\left(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma}\right)\\ \times\exp\left[\mathrm{i}(\kappa+k+q)\cdot x-\mathrm{i}(\kappa+k'+q')\cdot x'\right]\\ +\left(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma}\right)\left(mc^2+\hbar c\boldsymbol{\kappa}\cdot\boldsymbol{\gamma}+\gamma^0E(\boldsymbol{\kappa})\right)\left(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma}\right)\\ \times\exp\left[\mathrm{i}(\kappa+k-q')\cdot x-\mathrm{i}(\kappa+k'-q)\cdot x'\right]\Big]u_s(\boldsymbol{k}).\end{aligned}\tag{21.94}$$

We can simplify $S_{fi}=S^{(1)}_{fi}+S^{(3)}_{fi}$ by switching $x\leftrightarrow x'$ in $S^{(3)}_{fi}$ and taking into

account that

$$\begin{aligned}
&\int d^4\kappa \,\frac{mc^2-\hbar c\gamma\cdot\kappa}{\kappa^2+(m^2c^2/\hbar^2)-\mathrm{i}\epsilon}\exp(\mathrm{i}\kappa\cdot x)\\
&=-\int d^3\boldsymbol{\kappa}\int d\kappa^0\,\frac{\exp(\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{x})(mc^2-\hbar c\gamma\cdot\kappa)\exp(-\mathrm{i}\kappa^0 ct)}{[\kappa^0-(\omega(\boldsymbol{\kappa})/c)+\mathrm{i}\epsilon][\kappa^0+(\omega(\boldsymbol{\kappa})/c)-\mathrm{i}\epsilon]}\\
&=2\pi\mathrm{i}c\Theta(t)\int d^3\boldsymbol{\kappa}\,\exp(\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{x})\frac{mc^2-\hbar c\boldsymbol{\kappa}\cdot\boldsymbol{\gamma}-\gamma^0E(\boldsymbol{\kappa})}{2\omega(\boldsymbol{\kappa})}\exp(-\mathrm{i}\omega(\boldsymbol{\kappa})t)\\
&\quad-2\pi\mathrm{i}c\Theta(-t)\int d^3\boldsymbol{\kappa}\,\exp(\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{x})\frac{mc^2-\hbar c\boldsymbol{\kappa}\cdot\boldsymbol{\gamma}+\gamma^0E(\boldsymbol{\kappa})}{-2\omega(\boldsymbol{\kappa})}\exp(\mathrm{i}\omega(\boldsymbol{\kappa})t)\\
&=\mathrm{i}\pi c\Theta(t)\int\frac{d^3\boldsymbol{\kappa}}{\omega(\boldsymbol{\kappa})}(mc^2-\hbar c\gamma\cdot\kappa)\exp(\mathrm{i}\kappa\cdot x)\Big|_{\kappa^0=\omega(\boldsymbol{\kappa})/c}\\
&\quad+\mathrm{i}\pi c\Theta(-t)\int\frac{d^3\boldsymbol{\kappa}}{\omega(\boldsymbol{\kappa})}(mc^2+\hbar c\gamma\cdot\kappa)\exp(-\mathrm{i}\kappa\cdot x)\Big|_{\kappa^0=\omega(\boldsymbol{\kappa})/c}.
\end{aligned}\tag{21.95}$$

This yields the total scattering matrix element in the form

$$\begin{aligned}
S_{fi}=&\int d^4\kappa\int d^4x\int d^4x'\,\frac{\mathrm{i}e^2}{4(2\pi)^{10}\epsilon_0\hbar^2c\sqrt{|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k})E(\boldsymbol{k}')}}\\
&\times\overline{u}_{s'}(\boldsymbol{k}')\Big[(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\,\frac{mc-\hbar\gamma\cdot\kappa}{\kappa^2+(m^2c^2/\hbar^2)-\mathrm{i}\epsilon}\,(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma})\\
&\times\exp\left[\mathrm{i}(\kappa-k'-q')\cdot x+\mathrm{i}(k+q-\kappa)\cdot x'\right]\\
&+(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,\frac{mc-\hbar\gamma\cdot\kappa}{\kappa^2+(m^2c^2/\hbar^2)-\mathrm{i}\epsilon}\,(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\\
&\times\exp\left[\mathrm{i}(\kappa-k'+q)\cdot x+\mathrm{i}(k-q'-\kappa)\cdot x'\right]\Big]u_s(\boldsymbol{k}).
\end{aligned}$$

After performing the trivial integrations, we find

$$\begin{aligned}
S_{fi}=&\,\delta(k'+q'-k-q)\frac{\mathrm{i}e^2}{16\pi^2\epsilon_0\hbar^2c\sqrt{|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k})E(\boldsymbol{k}')}}\\
&\times\overline{u}_{s'}(\boldsymbol{k}')\Big[(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\,\frac{mc-\hbar\gamma\cdot(k+q)}{(k+q)^2+(m^2c^2/\hbar^2)-\mathrm{i}\epsilon}\,(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma})\\
&+(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,\frac{mc-\hbar\gamma\cdot(k-q')}{(k-q')^2+(m^2c^2/\hbar^2)-\mathrm{i}\epsilon}\,(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\Big]u_s(\boldsymbol{k}).
\end{aligned}\tag{21.96}$$

The first contribution to the amplitude corresponds to absorption of a photon with wave vector q followed by emission of a photon with wave vector q', see Figure 21.2, while the second contribution to the amplitude corresponds to emission of the photon with wave vector q' before absorption of the photon with wave vector q as shown in Figure 21.3.

The denominators in (21.96) can be simplified by noting that $k^2+(m^2c^2/\hbar^2)=0$, $q^2=q'^2=0$, and

$$k\cdot q=\boldsymbol{k}\cdot\boldsymbol{q}-|\boldsymbol{q}|\sqrt{\boldsymbol{k}^2+(m^2c^2/\hbar^2)}<0.$$

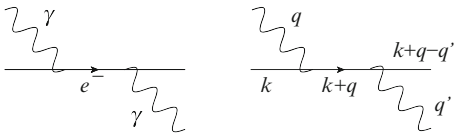


Figure 21.2: Absorption of the incoming photon with momentum $\hbar\boldsymbol{q}$ before emission of the outgoing photon with momentum $\hbar\boldsymbol{q}'$. The virtual intermediate electron has 4-momentum $\hbar(k+q)$. The left panel uses particle labels and the right panel uses momentum labels.

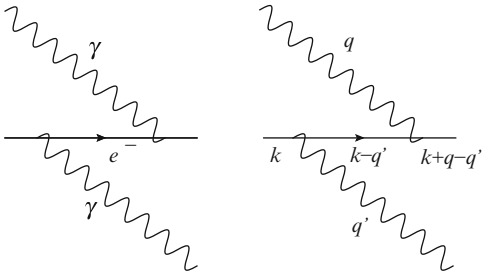


Figure 21.3: Emission of the outgoing photon with momentum $\hbar\boldsymbol{q}'$ before absorption of the incoming photon with momentum $\hbar\boldsymbol{q}$. The virtual intermediate electron has 4-momentum $\hbar(k-q')$.

This yields with the definition $\alpha = e^2/(4\pi\epsilon_0\hbar c)$ of Sommerfeld's fine structure constant the result

$$S_{fi} = \delta(k'+q'-k-q)\frac{\mathrm{i}\alpha}{8\pi\hbar\sqrt{|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k})E(\boldsymbol{k}')}}$$

$$\times\overline{u}_{s'}(\boldsymbol{k}')\Big[\,(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\,\frac{mc-\hbar\gamma\cdot(k+q)}{k\cdot q}\,(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\gamma})$$

$$-\,(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,\frac{mc-\hbar\gamma\cdot(k-q')}{k\cdot q'}\,(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\,\Big]u_s(\boldsymbol{k}). \tag{21.97}$$

The spin and helicity polarized differential scattering cross section then follows from (21.87),

$$v d\sigma_{\boldsymbol{k},s;\boldsymbol{q},\alpha\to\boldsymbol{k}',s';\boldsymbol{q}',\alpha'} = c d^3\boldsymbol{k}' d^3\boldsymbol{q}'\,\frac{\alpha^2\delta(k'+q'-k-q)}{16\hbar^2|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k})E(\boldsymbol{k}')}$$

$$\times\Big|\overline{u}_{s'}(\boldsymbol{k}')\Big[\,(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\,\frac{mc-\hbar\gamma\cdot(k+q)}{k\cdot q}\,(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\gamma})$$

$$-\,(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,\frac{mc-\hbar\gamma\cdot(k-q')}{k\cdot q'}\,(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\,\Big]u_s(\boldsymbol{k})\Big|^2. \tag{21.98}$$

Spin-polarized cross sections are usually of less physical interest than electron-photon cross sections which average over polarizations of initial electron states

and sum over the polarizations of the final electron states[9],

$$d\sigma_{\boldsymbol{k};\boldsymbol{q},\alpha\to\boldsymbol{k}';\boldsymbol{q}',\alpha'} = \frac{1}{2}\sum_{s,s'} d\sigma_{\boldsymbol{k},s;\boldsymbol{q},\alpha\to\boldsymbol{k}',s';\boldsymbol{q}',\alpha'}.$$

Use of the property (21.45)

$$\sum_s u_s(\boldsymbol{k})\overline{u}_s(\boldsymbol{k}) = mc^2 - \hbar c\gamma^\mu k_\mu\Big|_{k^0=\omega(\boldsymbol{k})/c}$$

and the relations $(\overline{u})^+ = \gamma^0 u$, $\gamma_\mu^+ = \gamma^0\gamma_\mu\gamma^0$ yields

$$\begin{aligned} v d\sigma_{\boldsymbol{k};\boldsymbol{q},\alpha\to\boldsymbol{k}';\boldsymbol{q}',\alpha'} &= d^3\boldsymbol{k}' d^3\boldsymbol{q}' \frac{\alpha^2 c^3 \delta(k'+q'-k-q)}{32\hbar^2|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k})E(\boldsymbol{k}')} \operatorname{tr}\Bigg[(mc - \hbar\gamma\cdot k') \\ &\times \Bigg((\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma}) \frac{mc - \hbar\gamma\cdot(k+q)}{k\cdot q} (\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma}) \\ &- (\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma}) \frac{mc - \hbar\gamma\cdot(k-q')}{k\cdot q'} (\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma}) \Bigg) (mc - \hbar\gamma\cdot k) \\ &\times \Bigg((\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma}) \frac{mc - \hbar\gamma\cdot(k+q)}{k\cdot q} (\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma}) \\ &- (\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma}) \frac{mc - \hbar\gamma\cdot(k-q')}{k\cdot q'} (\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma}) \Bigg) \Bigg]. \end{aligned} \tag{21.99}$$

This can be evaluated using the trace theorems for γ matrices from Appendix G. The full evaluation of $d\sigma_{\boldsymbol{k};\boldsymbol{q},\alpha\to\boldsymbol{k}';\boldsymbol{q}',\alpha'}$ needs in particular the trace theorems (G.19-G.21) for products of 4, 6 and 8 γ matrices.
We can simplify the evaluation in the rest frame of the initial electron,

$$k = \frac{1}{\hbar c}\begin{pmatrix} \sqrt{m^2c^4 + \hbar^2\boldsymbol{k}^2} \\ \hbar c\boldsymbol{k} \end{pmatrix} \Rightarrow \frac{mc}{\hbar}\begin{pmatrix} 1 \\ \boldsymbol{0} \end{pmatrix}.$$

We can also use that $\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{q} = \epsilon_\alpha(\boldsymbol{q})\cdot q = 0$ implies

$$(\gamma\cdot q)\,(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma}) = -\,(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,(\gamma\cdot q).$$

This reduces products according to

$$\begin{aligned} &(mc - \hbar\gamma\cdot(k+q))\,(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,(mc - \hbar\gamma\cdot k) \\ &= \left(mc + mc\gamma^0 - \hbar\gamma\cdot q\right)(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,mc\left(1+\gamma^0\right) \\ &= (\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma})\left(mc - mc\gamma^0 + \hbar\gamma\cdot q\right)mc\left(1+\gamma^0\right) \\ &= m\hbar c\,(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,(\gamma\cdot q)\left(1+\gamma^0\right). \end{aligned}$$

[9]However, spin polarized cross sections for electron scattering will likely become important in the framework of spintronics and spin based quantum computing.

The resulting cross section in the rest frame of the electron before scattering is

$$d\sigma_{\mathbf{0};\boldsymbol{q},\alpha\to\boldsymbol{k}';\boldsymbol{q}',\alpha'} = d^3\boldsymbol{k}' d^3\boldsymbol{q}' \frac{\alpha^2\hbar^2\delta(k'+q'-k-q)}{32m^2c|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k}')}\,\mathrm{tr}\Bigg[(mc-\hbar\gamma\cdot k')$$
$$\times\left((\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\,(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,\frac{\gamma\cdot q}{|\boldsymbol{q}|}+(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\,\frac{\gamma\cdot q'}{|\boldsymbol{q}'|}\right)\left(1+\gamma^0\right)$$
$$\times\left(\frac{\gamma\cdot q}{|\boldsymbol{q}|}\,(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\gamma})\,(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})+\frac{\gamma\cdot q'}{|\boldsymbol{q}'|}\,(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{\gamma})\,(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\gamma})\right)\Bigg]. \quad (21.100)$$

Traces over products of an odd number of γ matrices vanish. The terms under the trace proportional to mc^2 contain products of six γ matrices, but two of these products vanish due to $(\gamma\cdot q)^2 = -q^2 = 0$ and $(\gamma\cdot q')^2 = -q'^2 = 0$. The remaining two terms involving six γ matrices turn out to yield the same result, such that the contribution to the trace term from products of six γ matrices is

$$tr_6 = \frac{8mc}{|\boldsymbol{q}||\boldsymbol{q}'|}\Big(q\cdot q' - 2(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))^2 q\cdot q'$$
$$+2(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{q}')(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{q})\Big). \quad (21.101)$$

For the traces over products of eight γ matrices, we observe that those which contain the products $(\gamma\cdot q)\gamma^0(\gamma\cdot q)$ or $(\gamma\cdot q')\gamma^0(\gamma\cdot q')$ can be simplified to products of six γ matrices due to

$$\gamma^\mu\gamma^0\gamma^\nu q_\mu q_\nu = \left(-2\eta^{\mu 0}\gamma^\nu - \gamma^0\gamma^\mu\gamma^\nu\right) q_\mu q_\nu = -2|\boldsymbol{q}|\gamma^\nu q_\nu.$$

This yields for the sum of those terms which contain the products $(\gamma\cdot q)\gamma^0(\gamma\cdot q)$ or $(\gamma\cdot q')\gamma^0(\gamma\cdot q')$ the result

$$tr_{8a} = \frac{8\hbar}{|\boldsymbol{q}|}\Big(2(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{k}')(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{q}) - k'\cdot q\Big)$$
$$+\frac{8\hbar}{|\boldsymbol{q}'|}\Big(2(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{k}')(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{q}') - k'\cdot q'\Big),$$

and after substitution of $k' = k + q - q'$,

$$tr_{8a} = 16mc + \frac{8\hbar}{|\boldsymbol{q}|}\Big(q\cdot q' + 2(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{q})^2\Big)$$
$$-\frac{8\hbar}{|\boldsymbol{q}'|}\Big(q\cdot q' + 2(\boldsymbol{\epsilon}_{\alpha}(\boldsymbol{q})\cdot\boldsymbol{q}')^2\Big). \quad (21.102)$$

The traces over products of eight γ matrices which contain terms $(\gamma\cdot q)\gamma^0(\gamma\cdot q')$ or $(\gamma\cdot q')\gamma^0(\gamma\cdot q)$ can also be reduced to traces over products of six γ matrices by using the fact that γ^0 can only by contracted with one of the three γ

matrices in products with 4-vectors. This yields after a bit of calculation and after substitution of $k' = k + q - q'$,

$$\begin{aligned} tr_{8b} = {} & 16mc\Big(2(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))^2 - 1\Big) - \frac{8mc}{|\boldsymbol{q}||\boldsymbol{q}'|}\Big(q\cdot q' \\ & -2(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))^2 q\cdot q' + 2(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{q}')(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{q})\Big) \\ & -16\frac{\hbar}{|\boldsymbol{q}|}(\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}')\cdot\boldsymbol{q})^2 + 16\frac{\hbar}{|\boldsymbol{q}'|}(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{q}')^2. \end{aligned} \tag{21.103}$$

The total trace term is therefore

$$\begin{aligned} tr &= tr_6 + tr_{8a} + tr_{8b} \\ &= 32mc(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))^2 + 8\hbar\left(\frac{1}{|\boldsymbol{q}|} - \frac{1}{|\boldsymbol{q}'|}\right) q\cdot q', \end{aligned}$$

and combining all the terms yields

$$\begin{aligned} d\sigma_{\mathbf{0};\boldsymbol{q},\alpha\to\boldsymbol{k}';\boldsymbol{q}',\alpha'} &= d^3\boldsymbol{k}' d^3\boldsymbol{q}' \frac{\alpha^2\hbar^2\delta(k'+q'-k-q)}{4m^2c|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k}')} \\ \times \left[4mc(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))^2 + \hbar\left(\frac{1}{|\boldsymbol{q}|} - \frac{1}{|\boldsymbol{q}'|}\right) q\cdot q'\right]. \end{aligned} \tag{21.104}$$

The product $q\cdot q'$ is directly related to the photon scattering angle,

$$q\cdot q' = -|\boldsymbol{q}||\boldsymbol{q}'|\,(1-\cos\theta).$$

However, energy and momentum conservation also imply

$$q\cdot q' = -\frac{1}{2}(q-q')^2 = -\frac{1}{2}(k'-k)^2 = \frac{m^2c^2}{\hbar^2} - \frac{mc}{\hbar}k'^0 = \frac{mc}{\hbar}\,(|\boldsymbol{q}'| - |\boldsymbol{q}|).$$

The relation between scattering angle and scattered photon wave number is therefore

$$\cos\theta = 1 - \frac{mc}{\hbar}\left(\frac{1}{|\boldsymbol{q}'|} - \frac{1}{|\boldsymbol{q}|}\right), \quad |\boldsymbol{q}'| = \frac{mc|\boldsymbol{q}|}{mc + \hbar|\boldsymbol{q}|\,(1-\cos\theta)}. \tag{21.105}$$

This is of course nothing but the Compton relation (1.11) for the wavelength of the scattered photon in terms of the scattering angle,

$$\lambda' = \lambda + \frac{h}{mc}\,(1-\cos\theta).$$

The four-dimensional δ function

$$\begin{aligned} \delta(k'+q'-k-q) = {} & \delta\Big(\sqrt{\boldsymbol{k}'^2 + (m^2c^2/\hbar^2)} + |\boldsymbol{q}'| - (mc/\hbar) - |\boldsymbol{q}|\Big) \\ & \times\delta(\boldsymbol{k}'+\boldsymbol{q}'-\boldsymbol{q}) \end{aligned}$$

reduces the six-dimensional final state measure $d^3\boldsymbol{k}' d^3\boldsymbol{q}'$ to the two-dimensional measure $d\Omega(\hat{\boldsymbol{q}}') \equiv d\Omega$ over direction of the scattered photon after integration

over $d^3\boldsymbol{k}'$ and $d|\boldsymbol{q}'|$. We include already the factor $|\boldsymbol{q}'|E(\boldsymbol{k}')$ in the denominator in equation (21.104) in the calculation:

$$\begin{aligned}
&\int d^3\boldsymbol{k}' \int_0^\infty d|\boldsymbol{q}'| \, \frac{|\boldsymbol{q}'|}{E(\boldsymbol{k}')} f(|\boldsymbol{q}'|)\delta(k'+q'-k-q) \\
&= \int_0^\infty d|\boldsymbol{q}'| \, \frac{|\boldsymbol{q}'| f(|\boldsymbol{q}'|)}{c\sqrt{\hbar^2|\boldsymbol{q}'|^2+\hbar^2|\boldsymbol{q}|^2-2\hbar^2|\boldsymbol{q}'||\boldsymbol{q}|\cos\theta+m^2c^2}} \\
&\times\delta\Big(\sqrt{|\boldsymbol{q}'|^2+|\boldsymbol{q}|^2-2|\boldsymbol{q}'||\boldsymbol{q}|\cos\theta+(m^2c^2/\hbar^2)}+|\boldsymbol{q}'|-(mc/\hbar)-|\boldsymbol{q}|\Big) \\
&= \frac{1}{c}\left[\frac{|\boldsymbol{q}'| f(|\boldsymbol{q}'|)}{mc+\hbar|\boldsymbol{q}|(1-\cos\theta)}\right]_{|\boldsymbol{q}'|=mc|\boldsymbol{q}|/[mc+\hbar|\boldsymbol{q}|(1-\cos\theta)]} \\
&= \frac{m|\boldsymbol{q}|}{\left[mc+\hbar|\boldsymbol{q}|\,(1-\cos\theta)\right]^2} f\left(\frac{mc|\boldsymbol{q}|}{mc+\hbar|\boldsymbol{q}|\,(1-\cos\theta)}\right).
\end{aligned}$$

This yields the Klein-Nishina cross section

$$\begin{aligned}
d\sigma_{\mathbf{0};\boldsymbol{q},\alpha\to\boldsymbol{q}-\boldsymbol{q}';\boldsymbol{q}',\alpha'} &= d\Omega \frac{\alpha^2\hbar^2}{4mc\left[mc+\hbar|\boldsymbol{q}|\,(1-\cos\theta)\right]^2} \\
&\times\left(4mc(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))^2+\frac{\hbar^2|\boldsymbol{q}|^2\,(1-\cos\theta)^2}{mc+\hbar|\boldsymbol{q}|\,(1-\cos\theta)}\right). \qquad (21.106)
\end{aligned}$$

Averaging over the initial photon polarization and summing over the final polarization (18.78) yields the unpolarized differential cross section

$$\begin{aligned}
d\sigma_{\mathbf{0};\boldsymbol{q}\to\boldsymbol{q}-\boldsymbol{q}';\boldsymbol{q}'} &= \frac{1}{2}\sum_{\alpha,\alpha'} d\sigma_{\mathbf{0};\boldsymbol{q},\alpha\to\boldsymbol{q}-\boldsymbol{q}';\boldsymbol{q}',\alpha'} = d\Omega \frac{\alpha^2\hbar^2}{2mc\left[mc+\hbar|\boldsymbol{q}|\,(1-\cos\theta)\right]^2} \\
&\times\left(mc(1+\cos^2\theta)+\frac{\hbar^2|\boldsymbol{q}|^2\,(1-\cos\theta)^2}{mc+\hbar|\boldsymbol{q}|\,(1-\cos\theta)}\right). \qquad (21.107)
\end{aligned}$$

The resulting total cross section is

$$\begin{aligned}
\sigma_{\mathbf{0};\boldsymbol{q}\to\boldsymbol{q}-\boldsymbol{q}';\boldsymbol{q}'} &= \frac{\pi\alpha^2}{mc\hbar|\boldsymbol{q}|^3}\left[2\hbar|\boldsymbol{q}|\frac{2(mc)^3+8(mc)^2\hbar|\boldsymbol{q}|+9mc(\hbar|\boldsymbol{q}|)^2+(\hbar|\boldsymbol{q}|)^3}{(mc+2\hbar|\boldsymbol{q}|)^2}\right. \\
&\left.-\left[2(mc)^2+2mc\hbar|\boldsymbol{q}|-(\hbar|\boldsymbol{q}|)^2\right]\ln\left(1+\frac{2\hbar|\boldsymbol{q}|}{mc}\right)\right]. \qquad (21.108)
\end{aligned}$$

Photons below the hard X-ray regime satisfy $\hbar|\boldsymbol{q}| \ll mc$. This limit is also often denoted as the non-relativistic limit of Compton scattering because the kinetic energy imparted on the recoiling electron is small in this case,

$$\hbar^2(\boldsymbol{q}-\boldsymbol{q}')^2 \simeq 2\hbar^2\boldsymbol{q}^2\,(1-\cos\theta) \ll m^2c^2.$$

The cross section in the non-relativistic limit yields the Thomson cross section (18.79,18.80) for photon scattering,

$$\frac{d\sigma_{\mathbf{0};\boldsymbol{q},\alpha\to\boldsymbol{q}-\boldsymbol{q}';\boldsymbol{q}',\alpha'}}{d\Omega} = \left(\frac{\alpha\hbar}{mc}\right)^2 (\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))^2,$$

$$\frac{d\sigma_{\mathbf{0};\boldsymbol{q}\to\boldsymbol{q}-\boldsymbol{q}';\boldsymbol{q}'}}{d\Omega} = \left(\frac{\alpha\hbar}{mc}\right)^2 \frac{1+\cos^2\theta}{2},$$

$$\sigma_{\mathbf{0};\boldsymbol{q}\to\boldsymbol{q}-\boldsymbol{q}';\boldsymbol{q}'} = \frac{8\pi}{3}\left(\frac{\alpha\hbar}{mc}\right)^2 \equiv \sigma_T = 6.652\times 10^{-9}\,\text{Å}^2 = 0.6652\,\text{barn}. \quad (21.109)$$

The unpolarized differential scattering cross section (21.107) for Compton scattering is displayed for various photon energies in Figure 21.4. Forward scattering is energy indepedent, but scattering in other directions is suppressed with energy.

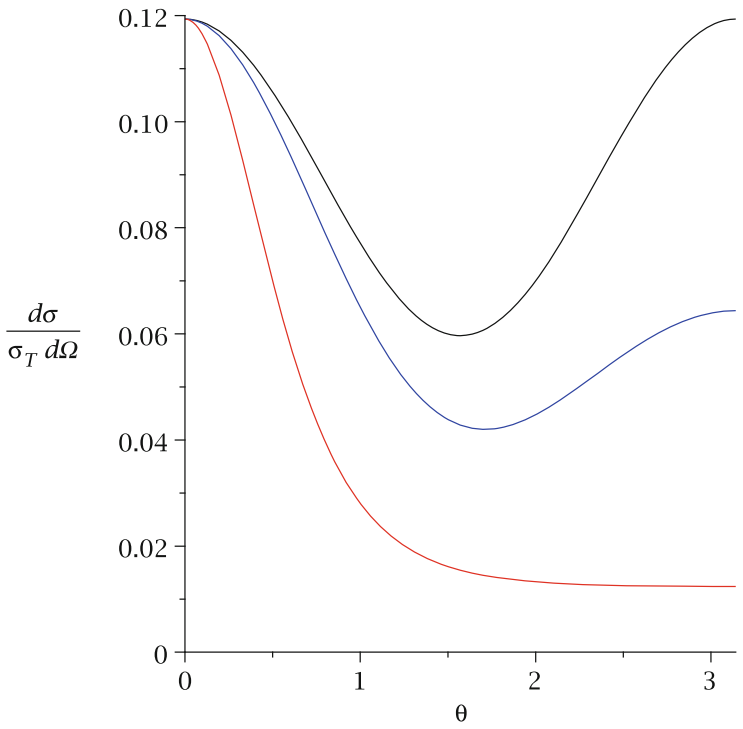


Figure 21.4: The differential scattering cross section (21.107) for scattering angle $0 \le \theta \le \pi$. The energy of the incident photon is $E_\gamma = 0$ (top black curve), $E_\gamma = 0.2mc^2$ (center blue curve) and $E_\gamma = 2mc^2$ (lower red curve).

The energy dependence of the total Compton scattering cross section (21.108) is displayed in Figure 21.5.

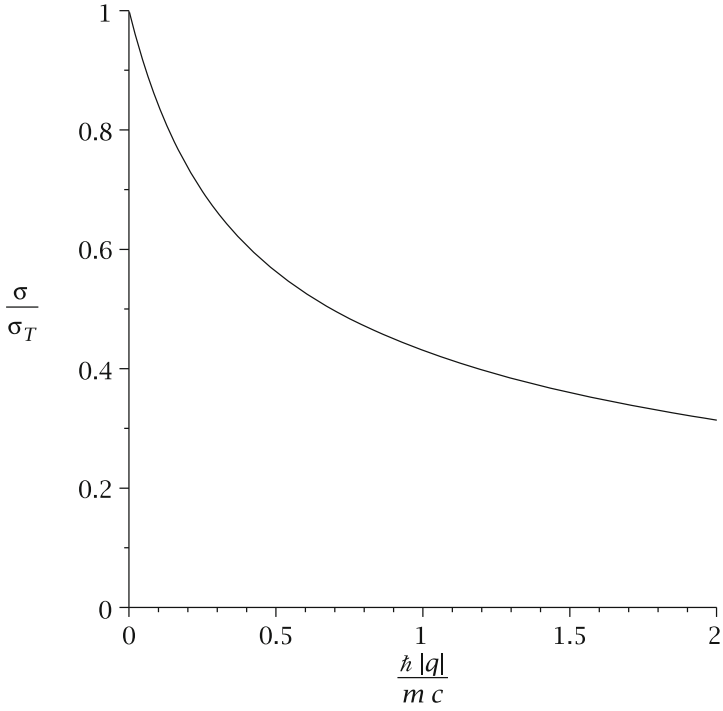


Figure 21.5: The total Compton scattering cross section (21.108) in units of the Thomson cross section (21.109) for incident photon energy $0 < E_\gamma < 2mc^2$.

21.8 Møller scattering

The leading order scattering cross section for electron-electron scattering was calculated in the framework of quantum electrodynamics by C. Møller[10].
The Hamiltonian (21.68) in Coulomb gauge $\boldsymbol{\nabla} \cdot \boldsymbol{A} = 0$ for the photon field is

$$H = H_0 + H_I + H_C, \tag{21.110}$$

with the electron-photon interaction term

$$H_I \equiv H_{e\gamma} = ec \int d^3\boldsymbol{x}\, \overline{\Psi}(\boldsymbol{x}, t)\boldsymbol{\gamma} \cdot \boldsymbol{A}(\boldsymbol{x}, t)\Psi(\boldsymbol{x}, t)$$

and the Coulomb interaction term

$$H_C = \frac{e^2}{8\pi\epsilon_0} \sum_{ss'} \int d^3\boldsymbol{x} \int d^3\boldsymbol{x}'\, \Psi_s^+(\boldsymbol{x}, t)\Psi_{s'}^+(\boldsymbol{x}', t) \frac{1}{|\boldsymbol{x} - \boldsymbol{x}'|} \Psi_{s'}(\boldsymbol{x}', t)\Psi_s(\boldsymbol{x}, t).$$

[10] C. Møller, Annalen Phys. 406, 531 (1932).

The corresponding Hamiltonian on the states in the interaction picture is therefore

$$H_D(t) = ec\sum_s \int d^3\boldsymbol{x}\,\overline{\Psi}_s(\boldsymbol{x},t)\boldsymbol{\gamma}\cdot\boldsymbol{A}(\boldsymbol{x},t)\Psi_s(\boldsymbol{x},t)$$
$$+\frac{e^2}{8\pi\epsilon_0}\sum_{ss'}\int d^3\boldsymbol{x}\int d^3\boldsymbol{x}'\,\Psi_s^+(\boldsymbol{x},t)\Psi_{s'}^+(\boldsymbol{x}',t)\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\Psi_{s'}(\boldsymbol{x}',t)\Psi_s(\boldsymbol{x},t)$$

with the freely evolving field operators $\boldsymbol{A}(\boldsymbol{x},t) \equiv \boldsymbol{A}_D(\boldsymbol{x},t)$ (18.20) and $\Psi(\boldsymbol{x},t) \equiv \Psi_D(\boldsymbol{x},t)$ (21.49) of the interaction picture.
The scattering matrix element for electron-electron scattering

$$S_{fi} \equiv S_{\boldsymbol{k}_1',s_1';\boldsymbol{k}_2',s_2'|\boldsymbol{k}_1,s_1;\boldsymbol{k}_2,s_2}$$
$$= \langle \boldsymbol{k}_1',s_1';\boldsymbol{k}_2',s_2'|\mathrm{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty}dt\,H_D(t)\right)|\boldsymbol{k}_1,s_1;\boldsymbol{k}_2,s_2\rangle$$

becomes in leading order $\mathcal{O}(e^2)$

$$S_{fi} = S_{fi,I} + S_{fi,C},$$

with the photon contribution

$$S_{fi,I} = -\frac{e^2}{\hbar^2}\int d^4x\int d^4x'\,\Theta(t-t')\langle \boldsymbol{k}_1',s_1';\boldsymbol{k}_2',s_2'|\overline{\Psi}(x)\boldsymbol{\gamma}\cdot\boldsymbol{A}(x)\Psi(x)$$
$$\times\overline{\Psi}(x')\boldsymbol{\gamma}\cdot\boldsymbol{A}(x')\Psi(x')|\boldsymbol{k}_1,s_1;\boldsymbol{k}_2,s_2\rangle$$

and the Coulomb term

$$S_{fi,C} = \frac{\mu_0 e^2}{8\pi\mathrm{i}\hbar}\langle \boldsymbol{k}_1',s_1';\boldsymbol{k}_2',s_2'|\int d^4x\int d^4x'\,\Psi^+(x)\Psi^+(x')$$
$$\times\frac{\delta(ct-ct')}{|\boldsymbol{x}-\boldsymbol{x}'|}\Psi(x')\Psi(x)|\boldsymbol{k}_1,s_1;\boldsymbol{k}_2,s_2\rangle.$$

We evaluate $S_{fi,I}$ first. Substitution of the relevant parts of the mode expansions yields (here we also use summation convention for the helicity and spin polarization indices)

$$S_{fi,I} = -\frac{e^2}{\hbar^2}\frac{\hbar\mu_0 c}{8(2\pi)^9}\int d^4x\int d^4x'\,\Theta(t-t')\int\frac{d^3\boldsymbol{q}_1'}{\sqrt{E(\boldsymbol{q}_1')}}\int\frac{d^3\boldsymbol{q}_2'}{\sqrt{E(\boldsymbol{q}_2')}}\int\frac{d^3\boldsymbol{q}'}{\sqrt{|\boldsymbol{q}'|}}$$
$$\times\int\frac{d^3\boldsymbol{q}_1}{\sqrt{E(\boldsymbol{q}_1)}}\int\frac{d^3\boldsymbol{q}_2}{\sqrt{E(\boldsymbol{q}_2)}}\int\frac{d^3\boldsymbol{q}}{\sqrt{|\boldsymbol{q}|}}\exp[\mathrm{i}(q'+q_2'-q_1')\cdot x-\mathrm{i}(q+q_1-q_2)\cdot x']$$
$$\times\overline{u}(\boldsymbol{q}_1',\sigma)\boldsymbol{\gamma}u(\boldsymbol{q}_2',\sigma')\cdot\boldsymbol{\epsilon}_\beta(\boldsymbol{q}')\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\overline{u}(\boldsymbol{q}_1,s)\boldsymbol{\gamma}u(\boldsymbol{q}_2,s')\langle 0|b(\boldsymbol{k}_1',s_1')b(\boldsymbol{k}_2',s_2')$$
$$\times b^+(\boldsymbol{q}_1',\sigma)b(\boldsymbol{q}_2',\sigma')a_\beta(\boldsymbol{q}')a_\alpha^+(\boldsymbol{q})b^+(\boldsymbol{q}_1,s)b(\boldsymbol{q}_2,s')b^+(\boldsymbol{k}_2,s_2)b^+(\boldsymbol{k}_1,s_1)|0\rangle.$$

Elimination of the photon operators yields

$$
\begin{aligned}
S_{fi,I} &= \frac{\mu_0 e^2 c}{8(2\pi)^9\hbar}\int d^4x\int d^4x'\,\Theta(t-t')\int\frac{d^3\boldsymbol{q}_1'}{\sqrt{E(\boldsymbol{q}_1')}}\int\frac{d^3\boldsymbol{q}_2'}{\sqrt{E(\boldsymbol{q}_2')}}\int\frac{d^3\boldsymbol{q}}{|\boldsymbol{q}|}\\
&\times\int\frac{d^3\boldsymbol{q}_1}{\sqrt{E(\boldsymbol{q}_1)}}\int\frac{d^3\boldsymbol{q}_2}{\sqrt{E(\boldsymbol{q}_2)}}\exp[\mathrm{i}(q+q_2'-q_1')\cdot x-\mathrm{i}(q+q_1-q_2)\cdot x']\\
&\times\overline{u}(\boldsymbol{q}_1',\sigma)\boldsymbol{\gamma}u(\boldsymbol{q}_2',\sigma')\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\overline{u}(\boldsymbol{q}_1,s)\boldsymbol{\gamma}u(\boldsymbol{q}_2,s')\langle 0|b(\boldsymbol{k}_1',s_1')b(\boldsymbol{k}_2',s_2')\\
&\times b^+(\boldsymbol{q}_1',\sigma)b^+(\boldsymbol{q}_1,s)b(\boldsymbol{q}_2',\sigma')b(\boldsymbol{q}_2,s')b^+(\boldsymbol{k}_2,s_2)b^+(\boldsymbol{k}_1,s_1)|0\rangle,
\end{aligned}
$$

where fermionic operators were also re-ordered such that only the connected amplitude contributes. Evaluation of the fermionic operators yields

$$
\begin{aligned}
S_{fi,I} &= \frac{e^2}{8\hbar}\frac{\mu_0 c}{(2\pi)^9}\int d^4x\int d^4x'\int\frac{d^3\boldsymbol{q}}{|\boldsymbol{q}|}\,\frac{\Theta(t-t')\exp[\mathrm{i}q\cdot(x-x')]}{\sqrt{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)}}\\
&\times\Big[\overline{u}(\boldsymbol{k}_2',s_2')\boldsymbol{\gamma}u(\boldsymbol{k}_1,s_1)\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\overline{u}(\boldsymbol{k}_1',s_1')\boldsymbol{\gamma}u(\boldsymbol{k}_2,s_2)\\
&\times\Big(\exp[\mathrm{i}(k_1-k_2')\cdot x-\mathrm{i}(k_1'-k_2)\cdot x']+\exp[\mathrm{i}(k_2-k_1')\cdot x-\mathrm{i}(k_2'-k_1)\cdot x']\Big)\\
&\quad-\overline{u}(\boldsymbol{k}_1',s_1')\boldsymbol{\gamma}u(\boldsymbol{k}_1,s_1)\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\overline{u}(\boldsymbol{k}_2',s_2')\boldsymbol{\gamma}u(\boldsymbol{k}_2,s_2)\\
&\times\Big(\exp[\mathrm{i}(k_1-k_1')\cdot x-\mathrm{i}(k_2'-k_2)\cdot x']\\
&\quad+\exp[\mathrm{i}(k_2-k_2')\cdot x-\mathrm{i}(k_1'-k_1)\cdot x']\Big)\Big].
\end{aligned}
$$

This yields after changing the integration variables $x\leftrightarrow x'$ in the second and fourth term

$$
\begin{aligned}
S_{fi,I} &= \frac{e^2}{8\hbar}\frac{\mu_0 c}{(2\pi)^9}\frac{1}{\sqrt{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)}}\int d^4x\int d^4x'\int\frac{d^3\boldsymbol{q}}{|\boldsymbol{q}|}\\
&\times\Big(\overline{u}(\boldsymbol{k}_2',s_2')\boldsymbol{\gamma}u(\boldsymbol{k}_1,s_1)\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\overline{u}(\boldsymbol{k}_1',s_1')\boldsymbol{\gamma}u(\boldsymbol{k}_2,s_2)\\
&\times\exp[\mathrm{i}(k_1-k_2')\cdot x+\mathrm{i}(k_2-k_1')\cdot x']\\
&-\overline{u}(\boldsymbol{k}_1',s_1')\boldsymbol{\gamma}u(\boldsymbol{k}_1,s_1)\cdot\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\overline{u}(\boldsymbol{k}_2',s_2')\boldsymbol{\gamma}u(\boldsymbol{k}_2,s_2)\\
&\times\exp[\mathrm{i}(k_1-k_1')\cdot x+\mathrm{i}(k_2-k_2')\cdot x']\Big)\\
&\times\Big(\Theta(t-t')\exp[\mathrm{i}q\cdot(x-x')]+\Theta(t'-t)\exp[\mathrm{i}q\cdot(x'-x)]\Big).
\end{aligned}
$$

We can use the following equation with $\omega(\boldsymbol{q})=c\sqrt{\boldsymbol{q}^2+(m^2c^2/\hbar^2)}$

$$
\begin{aligned}
&\int d^4q\,\frac{\exp(\mathrm{i}q\cdot x)}{q^2+(m^2c^2/\hbar^2)-\mathrm{i}\epsilon}=-\int d^3\boldsymbol{q}\int d\omega\,\frac{c\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{x})\exp(-\mathrm{i}\omega t)}{[\omega-\omega(\boldsymbol{q})+\mathrm{i}\epsilon][\omega+\omega(\boldsymbol{q})-\mathrm{i}\epsilon]}\\
&=2\pi c\mathrm{i}\Theta(t)\int d^3\boldsymbol{q}\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{x})\frac{\exp(-\mathrm{i}\omega(\boldsymbol{q})t)}{2\omega(\boldsymbol{q})}\\
&\quad-2\pi c\mathrm{i}\Theta(-t)\int d^3\boldsymbol{q}\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{x})\frac{\exp(\mathrm{i}\omega(\boldsymbol{q})t)}{-2\omega(\boldsymbol{q})}\\
&=\mathrm{i}\pi c\Theta(t)\int\frac{d^3\boldsymbol{q}}{\omega(\boldsymbol{q})}\exp(\mathrm{i}q\cdot x)\Big|_{\omega=\omega(\boldsymbol{q})}+\mathrm{i}\pi c\Theta(-t)\int\frac{d^3\boldsymbol{q}}{\omega(\boldsymbol{q})}\exp(-\mathrm{i}q\cdot x)\Big|_{\omega=\omega(\boldsymbol{q})}
\end{aligned}
$$

to find

$$S_{fi,I} = \frac{\mu_0 e^2 c}{4\mathrm{i}\hbar(2\pi)^{10}} \frac{1}{\sqrt{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)}} \int d^4x \int d^4x' \int \frac{d^4q}{q^2 - \mathrm{i}\epsilon}$$
$$\times \Big(\overline{u}(\boldsymbol{k}_2', s_2')\boldsymbol{\gamma} u(\boldsymbol{k}_1, s_1) \cdot \boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\boldsymbol{\epsilon}_\alpha(\boldsymbol{q}) \cdot \overline{u}(\boldsymbol{k}_1', s_1')\boldsymbol{\gamma} u(\boldsymbol{k}_2, s_2)$$
$$\times \exp[\mathrm{i}(k_1 - k_2' + q)\cdot x + \mathrm{i}(k_2 - k_1' - q)\cdot x']$$
$$- \overline{u}(\boldsymbol{k}_1', s_1')\boldsymbol{\gamma} u(\boldsymbol{k}_1, s_1) \cdot \boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\boldsymbol{\epsilon}_\alpha(\boldsymbol{q}) \cdot \overline{u}(\boldsymbol{k}_2', s_2')\boldsymbol{\gamma} u(\boldsymbol{k}_2, s_2)$$
$$\times \exp[\mathrm{i}(k_1 - k_1' + q)\cdot x + \mathrm{i}(k_2 - k_2' - q)\cdot x'] \Big).$$

The integrations then yield

$$S_{fi,I} = \frac{\mu_0 e^2 c}{16\mathrm{i}\pi^2\hbar} \frac{\delta(k_1 + k_2 - k_1' - k_2')}{\sqrt{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)}}$$
$$\times \left(\frac{\overline{u}(\boldsymbol{k}_2', s_2')\boldsymbol{\gamma} u(\boldsymbol{k}_1, s_1) \cdot \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}_2' - \boldsymbol{k}_1)\boldsymbol{\epsilon}_\alpha(\boldsymbol{k}_2' - \boldsymbol{k}_1) \cdot \overline{u}(\boldsymbol{k}_1', s_1')\boldsymbol{\gamma} u(\boldsymbol{k}_2, s_2)}{(k_2' - k_1)^2 - \mathrm{i}\epsilon} \right.$$
$$\left. - \frac{\overline{u}(\boldsymbol{k}_1', s_1')\boldsymbol{\gamma} u(\boldsymbol{k}_1, s_1) \cdot \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}_1' - \boldsymbol{k}_1)\boldsymbol{\epsilon}_\alpha(\boldsymbol{k}_1' - \boldsymbol{k}_1) \cdot \overline{u}(\boldsymbol{k}_2', s_2')\boldsymbol{\gamma} u(\boldsymbol{k}_2, s_2)}{(k_1' - k_1)^2 - \mathrm{i}\epsilon} \right).$$

Taking into account the energy-momentum conserving δ function, the transversal projectors can e.g. be written as

$$\boldsymbol{\epsilon}_\alpha(\boldsymbol{k}_1' - \boldsymbol{k}_1) \otimes \boldsymbol{\epsilon}_\alpha(\boldsymbol{k}_1' - \boldsymbol{k}_1) = \underline{1} + \frac{(\boldsymbol{k}_1' - \boldsymbol{k}_1) \otimes (\boldsymbol{k}_2' - \boldsymbol{k}_2)}{(\boldsymbol{k}_1' - \boldsymbol{k}_1)^2}.$$

The Dirac equation implies

$$\overline{u}(\boldsymbol{k}', s')\boldsymbol{\gamma} \cdot (\boldsymbol{k}' - \boldsymbol{k}) u(\boldsymbol{k}, s) = \frac{E(\boldsymbol{k}') - E(\boldsymbol{k})}{\hbar c} \overline{u}(\boldsymbol{k}', s')\gamma^0 u(\boldsymbol{k}, s).$$

This yields the photon exchange contribution to the electron-electron scattering matrix element,

$$S_{fi,I} = \frac{\mu_0 c e^2}{16\mathrm{i}\pi^2\hbar} \frac{\delta(k_1 + k_2 - k_1' - k_2')}{\sqrt{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)}}$$
$$\times \left(\frac{\overline{u}(\boldsymbol{k}_2', s_2')\boldsymbol{\gamma} u(\boldsymbol{k}_1, s_1) \cdot \overline{u}(\boldsymbol{k}_1', s_1')\boldsymbol{\gamma} u(\boldsymbol{k}_2, s_2)}{(k_2' - k_1)^2 - \mathrm{i}\epsilon} \right.$$
$$- \frac{\overline{u}(\boldsymbol{k}_1', s_1')\boldsymbol{\gamma} u(\boldsymbol{k}_1, s_1) \cdot \overline{u}(\boldsymbol{k}_2', s_2')\boldsymbol{\gamma} u(\boldsymbol{k}_2, s_2)}{(k_1' - k_1)^2 - \mathrm{i}\epsilon}$$
$$- \frac{\overline{u}(\boldsymbol{k}_2', s_2')\gamma^0 u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_1', s_1')\gamma^0 u(\boldsymbol{k}_2, s_2)}{(k_2' - k_1)^2 - \mathrm{i}\epsilon} \frac{[E(\boldsymbol{k}_2') - E(\boldsymbol{k}_1)]^2}{\hbar^2 c^2 (\boldsymbol{k}_2' - \boldsymbol{k}_1)^2}$$
$$\left. + \frac{\overline{u}(\boldsymbol{k}_1', s_1')\gamma^0 u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_2', s_2')\gamma^0 u(\boldsymbol{k}_2, s_2)}{(k_1' - k_1)^2 - \mathrm{i}\epsilon} \frac{[E(\boldsymbol{k}_1') - E(\boldsymbol{k}_1)]^2}{\hbar^2 c^2 (\boldsymbol{k}_1' - \boldsymbol{k}_1)^2} \right). \quad (21.111)$$

For the evaluation of the Coulomb term, substitution of the mode expansions and evaluation of the operators in $S_{fi,C}$ yields

$$
\begin{aligned}
S_{fi,C} &= \frac{\mu_0 c e^2}{8\pi \mathrm{i}\hbar} \frac{1}{4(2\pi)^6 \sqrt{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)}} \int d^4x \int d^4x' \, \frac{\delta(ct-ct')}{|\boldsymbol{x}-\boldsymbol{x}'|} \\
&\times \Big(\overline{u}(\boldsymbol{k}_1', s_1')\gamma^0 u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_2', s_2')\gamma^0 u(\boldsymbol{k}_2, s_2) \exp[\mathrm{i}(k_2'-k_2)\cdot x' + \mathrm{i}(k_1'-k_1)\cdot x] \\
&- \overline{u}(\boldsymbol{k}_2', s_2')\gamma^0 u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_1', s_1')\gamma^0 u(\boldsymbol{k}_2, s_2) \exp[\mathrm{i}(k_1'-k_2)\cdot x' + \mathrm{i}(k_2'-k_1)\cdot x] \Big) \\
&= \frac{\mu_0 c e^2}{16\pi \mathrm{i}\hbar} \frac{1}{(2\pi)^6 \sqrt{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)}} \\
&\times \int d^4x \int d^3\boldsymbol{x}' \, \frac{\exp[\mathrm{i}(k_1'+k_2'-k_1-k_2)\cdot x]}{|\boldsymbol{x}-\boldsymbol{x}'|} \\
&\times \Big(\overline{u}(\boldsymbol{k}_1', s_1')\gamma^0 u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_2', s_2')\gamma^0 u(\boldsymbol{k}_2, s_2) \exp[\mathrm{i}(\boldsymbol{k}_2'-\boldsymbol{k}_2)\cdot(\boldsymbol{x}'-\boldsymbol{x})] \\
&- \overline{u}(\boldsymbol{k}_2', s_2')\gamma^0 u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_1', s_1')\gamma^0 u(\boldsymbol{k}_2, s_2) \exp[\mathrm{i}(\boldsymbol{k}_1'-\boldsymbol{k}_2)\cdot(\boldsymbol{x}'-\boldsymbol{x})] \Big).
\end{aligned}
$$

In the next step we use

$$
\int d^3\boldsymbol{x}' \frac{\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{x}')}{|\boldsymbol{x}'|} = \frac{4\pi}{\boldsymbol{q}^2}
$$

to find

$$
\begin{aligned}
S_{fi,C} &= \frac{\mu_0 c e^2}{16\pi^2 \mathrm{i}\hbar} \frac{\delta(k_1'+k_2'-k_1-k_2)}{\sqrt{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)}} \\
&\times \Bigg(\frac{\overline{u}(\boldsymbol{k}_1', s_1')\gamma^0 u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_2', s_2')\gamma^0 u(\boldsymbol{k}_2, s_2)}{(\boldsymbol{k}_2'-\boldsymbol{k}_2)^2} \\
&- \frac{\overline{u}(\boldsymbol{k}_2', s_2')\gamma^0 u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_1', s_1')\gamma^0 u(\boldsymbol{k}_2, s_2)}{(\boldsymbol{k}_2'-\boldsymbol{k}_1)^2} \Bigg).
\end{aligned}
$$

For the addition of $S_{fi,I}$ and $S_{fi,C}$, we observe

$$
\frac{1}{(\boldsymbol{k}'-\boldsymbol{k})^2} \left(\frac{[\omega(\boldsymbol{k}')-\omega(\boldsymbol{k})]^2}{c^2(k'-k)^2} + 1 \right) = \frac{1}{(k'-k)^2}
$$

to find

$$
\begin{aligned}
S_{fi} &= \mathrm{i}\frac{\mu_0 c e^2}{16\pi^2\hbar} \frac{\delta(k_1'+k_2'-k_1-k_2)}{\sqrt{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)}} \\
&\times \Bigg(\frac{\overline{u}(\boldsymbol{k}_1', s_1')\gamma^\mu u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_2', s_2')\gamma_\mu u(\boldsymbol{k}_2, s_2)}{(k_1'-k_1)^2} \\
&- \frac{\overline{u}(\boldsymbol{k}_2', s_2')\gamma^\mu u(\boldsymbol{k}_1, s_1)\overline{u}(\boldsymbol{k}_1', s_1')\gamma_\mu u(\boldsymbol{k}_2, s_2)}{(k_2'-k_1)^2} \Bigg) \\
&= -\mathrm{i}\mathcal{M}_{fi}\delta(k_1+k_2-k_1'-k_2'),
\end{aligned} \tag{21.112}
$$

where the last equation defines the scattering amplitude

$$\mathcal{M}_{fi} \equiv \mathcal{M}_{\boldsymbol{k}'_1,s'_1;\boldsymbol{k}'_2,s'_2|\boldsymbol{k}_1,s_1;\boldsymbol{k}_2,s_2}$$

for Møller scattering.
The two contributions to the scattering amplitude can be interpreted as virtual photon exchange with virtual photon 4-momentum $k_1 - k'_1$ or $k_1 - k'_2$, respectively see Figure 21.6. In the Coulomb gauge formalism used here the electron-electron Coulomb interaction corresponds to the timelike component of the virtual intermediate photons.

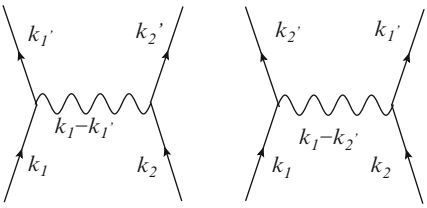


Figure 21.6: Contributions to the Møller scattering amplitude (21.112).

The scattering amplitude (21.112) yields the spin polarized differential cross section (21.88)

$$\begin{aligned} v d\sigma_{\boldsymbol{k}'_1,s'_1;\boldsymbol{k}'_2,s'_2|\boldsymbol{k}_1,s_1;\boldsymbol{k}_2,s_2} &= 4\pi^2 c \left|\mathcal{M}_{\boldsymbol{k}'_1,s'_1;\boldsymbol{k}'_2,s'_2|\boldsymbol{k}_1,s_1;\boldsymbol{k}_2,s_2}\right|^2 \\ &\quad \times \delta(k_1 + k_2 - k'_1 - k'_2) \frac{1}{2} d^3\boldsymbol{k}'_1 d^3\boldsymbol{k}'_2, \end{aligned}$$

where

$$v = \frac{c^3}{E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)} \sqrt{(\hbar^2 k_1 \cdot k_2)^2 - m^4 c^4} \tag{21.113}$$

is the relative speed (21.82) between the two electrons with momentum 4-vectors $\hbar k_1$ and $\hbar k_2$.
The differential cross section is often averaged over initial spin states and summed over final spin states,

$$d\sigma_{\boldsymbol{k}'_1;\boldsymbol{k}'_2|\boldsymbol{k}_1;\boldsymbol{k}_2} = \frac{1}{4} \sum_{s_1,s_2,s'_1,s'_2} d\sigma_{\boldsymbol{k}'_1,s'_1;\boldsymbol{k}'_2,s'_2|\boldsymbol{k}_1,s_1;\boldsymbol{k}_2,s_2}.$$

The property (21.45)

$$\sum_s u(\boldsymbol{k},s)\overline{u}(\boldsymbol{k},s) = mc^2 - \hbar c \gamma^\mu k_\mu \Big|_{k^0=\omega(\boldsymbol{k})/c}$$

yields

$$
\begin{aligned}
v d\sigma = & \frac{c}{2} d^3\boldsymbol{k}_1' d^3\boldsymbol{k}_2' \left(\frac{\mu_0 c e^2}{16\pi\hbar}\right)^2 \frac{\delta(k_1+k_2-k_1'-k_2')}{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)} \\
& \times \Bigg(\frac{1}{(k_1'-k_1)^4} \mathrm{tr}\left[\left(mc^2 - \hbar c\gamma\cdot k_1'\right)\gamma^\mu \left(mc^2 - \hbar c\gamma\cdot k_1\right)\gamma^\nu\right] \\
& \times \mathrm{tr}\left[\left(mc^2 - \hbar c\gamma\cdot k_2'\right)\gamma_\mu \left(mc^2 - \hbar c\gamma\cdot k_2\right)\gamma_\nu\right] \\
& + \frac{1}{(k_2'-k_1)^4} \mathrm{tr}\left[\left(mc^2 - \hbar c\gamma\cdot k_2'\right)\gamma^\mu \left(mc^2 - \hbar c\gamma\cdot k_1\right)\gamma^\nu\right] \\
& \times \mathrm{tr}\left[\left(mc^2 - \hbar c\gamma\cdot k_1'\right)\gamma_\mu \left(mc^2 - \hbar c\gamma\cdot k_2\right)\gamma_\nu\right] \\
& - \frac{2}{(k_1'-k_1)^2(k_2'-k_1)^2} \mathrm{tr}\left[\left(mc^2 - \hbar c\gamma\cdot k_2\right)\gamma^\mu \left(mc^2 - \hbar c\gamma\cdot k_2'\right)\right. \\
& \left. \times \gamma^\nu \left(mc^2 - \hbar c\gamma\cdot k_1\right)\gamma_\mu \left(mc^2 - \hbar c\gamma\cdot k_1'\right)\gamma_\nu\right] \Bigg), \qquad (21.114)
\end{aligned}
$$

where it is understood that all 4-momenta of electrons are on shell. The 4-momenta of the intermediate photons are then automatically off shell with dominant spacelike components, $(k'-k)^2 > 0$ (except in the zero momentum transfer limit $\boldsymbol{k}' = \boldsymbol{k}$).

The traces in equation (21.114) are readily evaluated using the contraction and trace theorems for γ matrices from Appendix G. This yields together with 4-momentum conservation $k_1' + k_2' = k_1 + k_2$ the result

$$
\begin{aligned}
v d\sigma = & c d^3\boldsymbol{k}_1' d^3\boldsymbol{k}_2' \left(\frac{e^2 c}{4\pi\epsilon_0\hbar}\right)^2 \frac{\delta(k_1+k_2-k_1'-k_2')}{E(\boldsymbol{k}_1')E(\boldsymbol{k}_2')E(\boldsymbol{k}_1)E(\boldsymbol{k}_2)} \\
& \times \Bigg(\frac{\hbar^4(k_1\cdot k_2)^2 + \hbar^4(k_1\cdot k_2')^2 + 2m^2c^2\hbar^2 k_1\cdot k_1' + 2m^4c^4}{(k_1'-k_1)^4} \\
& + \frac{\hbar^4(k_1\cdot k_2)^2 + \hbar^4(k_1\cdot k_1')^2 + 2m^2c^2\hbar^2 k_1\cdot k_2' + 2m^4c^4}{(k_2'-k_1)^4} \\
& + 2\,\frac{\hbar^4(k_1\cdot k_2)^2 + 2m^2c^2\hbar^2 k_1\cdot k_2}{(k_1'-k_1)^2(k_2'-k_1)^2} \Bigg). \qquad (21.115)
\end{aligned}
$$

We further evaluate the cross section through integration over $d^3\boldsymbol{k}_2'$ and $d|\boldsymbol{k}_1'|$ in the center of mass frame $\boldsymbol{k}_1 + \boldsymbol{k}_2 = \boldsymbol{0}$ of the colliding electrons. If we integrate over the final states $d^3\boldsymbol{k}_2'$ of one of the electrons to get a single-electron differential cross section $d\sigma/d\Omega$, we have to include a factor of 2 because we could just as well observe the electron with momentum $\boldsymbol{k}_2'$ being scattered into the direction $d\Omega$, see equation (21.90).

It is convenient to define $\boldsymbol{k} = \boldsymbol{k}_1$, $\boldsymbol{k}' = \boldsymbol{k}_1'$. The integration with the

energy-momentum δ function then yields

$$\int d^3\boldsymbol{k}_2' \int_0^\infty d|\boldsymbol{k}'|\,|\boldsymbol{k}'|^2 f(\boldsymbol{k},\boldsymbol{k}',\boldsymbol{k}_2')\delta(\boldsymbol{k}_2'+\boldsymbol{k}')$$
$$\times\delta\Big(2\sqrt{|\boldsymbol{k}'|^2+(mc/\hbar)^2}-2\sqrt{|\boldsymbol{k}|^2+(mc/\hbar)^2}\Big)$$
$$=\frac{|\boldsymbol{k}|}{2}\sqrt{|\boldsymbol{k}|^2+(mc/\hbar)^2}\,f(\boldsymbol{k},|\boldsymbol{k}|\hat{\boldsymbol{k}}',-|\boldsymbol{k}|\hat{\boldsymbol{k}}').$$

The scalar products in the center of mass frame are

$$k_1\cdot k_2=-2|\boldsymbol{k}|^2-(mc/\hbar)^2,$$

$$k_1\cdot k_1'=-|\boldsymbol{k}|^2(1-\cos\theta)-(mc/\hbar)^2,$$

$$k_1\cdot k_2'=-|\boldsymbol{k}|^2(1+\cos\theta)-(mc/\hbar)^2,$$

where θ is the angle between $\boldsymbol{k}$ and $\boldsymbol{k}'$. The relative speed (21.113) of the electrons in the center of mass frame is

$$v=\frac{2c\hbar|\boldsymbol{k}|}{\sqrt{\hbar^2|\boldsymbol{k}|^2+m^2c^2}}.$$

The differential scattering cross section is then with the factor of 2 from equation (21.90), and using the fine structure constant $\alpha=e^2/(4\pi\epsilon_0\hbar c)$,

$$\frac{d\sigma}{d\Omega}=\alpha^2\frac{\hbar^4k^4(3+\cos^2\theta)^2+m^2c^2(4\hbar^2k^2+m^2c^2)(1+3\cos^2\theta)}{4\hbar^2k^4(\hbar^2k^2+m^2c^2)\sin^4\theta}. \qquad (21.116)$$

This is symmetric under $\theta\to(\pi/2)-\theta$ with a minimum for scattering angle $\theta=\pi/2$ and divergences in forward and backward direction. This divergence in the zero momentum transfer limit is due to the vanishing photon mass, or in other words due to the infinite range of electromagnetic interactions. It is the same divergence which rendered the Rutherford cross section non-integrable. Equation (21.116) looks fairly complicated, but in terms of energy it essentially entails that Møller scattering is suppressed with kinetic energy K like K^{-2}: The low energy result for $K\simeq\hbar^2k^2/2m\ll mc^2$ is

$$\frac{d\sigma}{d\Omega}=\left(\frac{\alpha\hbar c}{4K\sin^2\theta}\right)^2(1+3\cos^2\theta),$$

and the high energy result for $K\simeq\hbar ck\gg mc^2$ is

$$\frac{d\sigma}{d\Omega}=\left(\frac{\alpha\hbar c}{2K}\frac{3+\cos^2\theta}{\sin^2\theta}\right)^2.$$

21.9 Problems

21.1 We have discussed the non-relativistic limit of the Klein-Gordon field in the case $|\langle b^+(\boldsymbol{k})\rangle| \ll |\langle a(\boldsymbol{k})\rangle|$ using the *ansatz* (21.14). However, there must also exist a non-relativistic limit for the anti-particles. How does the non-relativistic limit work in the case of negligible particle amplitude $|\langle a(\boldsymbol{k})\rangle| \ll |\langle b^+(\boldsymbol{k})\rangle|$?

21.2 Derive the Hamiltonian density $\mathcal{H}$ and the momentum density $\boldsymbol{\mathcal{P}}$ for the real Klein-Gordon field.

21.3 Calculate the non-relativistic limits for the Hamiltonian operator H and the momentum operator $\boldsymbol{P}$ of the real Klein-Gordon field.

21.4 Derive the energy-momentum tensor for QED with scalar matter (21.2),

$$\begin{aligned} T_\nu{}^\mu = &-\eta_\nu{}^\mu \hbar c^2 \left(\partial_\rho \phi^+ + \mathrm{i}\frac{q}{\hbar}\phi^+ A_\rho\right)\left(\partial^\rho \phi - \mathrm{i}\frac{q}{\hbar}A^\rho \phi\right) - \eta_\nu{}^\mu \frac{m^2c^4}{\hbar}\phi^+\phi \\ &-\eta_\nu{}^\mu \frac{1}{4\mu_0}F_{\rho\sigma}F^{\rho\sigma} + \hbar c^2 \left(\partial_\nu \phi^+ + \mathrm{i}\frac{q}{\hbar}\phi^+ A_\nu\right)\left(\partial^\mu \phi - \mathrm{i}\frac{q}{\hbar}A^\mu \phi\right) \\ &+\hbar c^2 \left(\partial^\mu \phi^+ + \mathrm{i}\frac{q}{\hbar}\phi^+ A^\mu\right)\left(\partial_\nu \phi - \mathrm{i}\frac{q}{\hbar}A_\nu \phi\right) + \frac{1}{\mu_0}F_{\nu\rho}F^{\mu\rho}. \end{aligned}$$

The corresponding densities of energy, momentum, and energy current are

$$\begin{aligned} \mathcal{H} = T^{00} &= \frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2 + \frac{m^2c^4}{\hbar}\phi^+\phi + \hbar\left(\dot{\phi}^+ - \mathrm{i}\frac{q}{\hbar}\phi^+\Phi\right)\left(\dot{\phi} + \mathrm{i}\frac{q}{\hbar}\Phi\phi\right) \\ &\quad +\hbar c^2 \left(\boldsymbol{\nabla}\phi^+ + \mathrm{i}\frac{q}{\hbar}\phi^+\boldsymbol{A}\right)\cdot\left(\boldsymbol{\nabla}\phi - \mathrm{i}\frac{q}{\hbar}\boldsymbol{A}\phi\right), \qquad (21.117) \\ \boldsymbol{\mathcal{P}} = \frac{1}{c}\boldsymbol{e}_i T^{i0} &= \epsilon_0 \boldsymbol{E}\times\boldsymbol{B} - \hbar\left(\dot{\phi}^+ - \mathrm{i}\frac{q}{\hbar}\phi^+\Phi\right)\left(\boldsymbol{\nabla}\phi - \mathrm{i}\frac{q}{\hbar}\boldsymbol{A}\phi\right) \\ &\quad -\hbar\left(\boldsymbol{\nabla}\phi^+ + \mathrm{i}\frac{q}{\hbar}\phi^+\boldsymbol{A}\right)\left(\dot{\phi} + \mathrm{i}\frac{q}{\hbar}\Phi\phi\right), \\ \boldsymbol{\mathcal{S}} &= c\boldsymbol{e}_i T^{0i} = c^2\boldsymbol{\mathcal{P}}. \end{aligned}$$

21.5 Show that the junction conditions (21.22) are necessary and sufficient to ensure that the Klein-Gordon equation holds at the step of the potential.

21.6 Calculate the boson number operator

$$N_b = \int d^3\boldsymbol{k}\left(a^+(\boldsymbol{k})a(\boldsymbol{k}) + b^+(\boldsymbol{k})b(\boldsymbol{k})\right)$$

for the free Klein-Gordon field in $\boldsymbol{x}$ representation.

21.7 Show that scattering of a Klein-Gordon field off a hard sphere yields the same result (11.29) as the non-relativistic Schrödinger theory, except that the definition $k = \sqrt{2mE}/\hbar$ (where E is the kinetic energy of the scattered particle) is replaced by

$$k = \frac{1}{\hbar c}\sqrt{\hbar^2\omega^2 - m^2c^4}.$$

The hard sphere is taken into account through a boundary condition of vanishing Klein-Gordon field on the surface of the sphere, like the condition on

the Schrödinger wave function in Section 11.3, i.e. we do not model it as a potential. We could think of the hard sphere in this case as arising from a hypothetical interaction which repels particles and anti-particles alike (just like gravity is equally attractive for particles and anti-particles).

21.8 You could also model an impenetrable wall for a Klein-Gordon field in the manner of the hard sphere of Poblem 7. Which wave function for the Klein-Gordon field do you get if the impenetrable wall prevents the field from entering the region $x > 0$? Why does this result not contradict the Klein paradox?

21.9 Calculate the current operator $\boldsymbol{J} = \int d^3\boldsymbol{x}\, \boldsymbol{j}$ for the free Dirac field in the Dirac representation.

21.10 Calculate the fermion number operator

$$N_f = \int d^3\boldsymbol{k} \sum_{s\in\{\downarrow,\uparrow\}} \left[b_s^+(\boldsymbol{k})b_s(\boldsymbol{k}) + d_s^+(\boldsymbol{k})d_s(\boldsymbol{k})\right]$$

for the free Dirac field in $\boldsymbol{x}$ representation.

21.11 Calculate the reflection and transmission coefficients for a Dirac field of charge q in the presence of a potential step $q\Phi(x) = V(x) = V\Theta(x)$. How do your results compare with the results for the Klein-Gordon field in Section 21.2?

21.12 Derive the limit (3.37) on the usability of (3.31) for free single-particle wave functions from equation (21.70). Show that at the distance d from the center of the wave packet the positron component cannot be neglected any more, $|\phi/\psi| \simeq 1$.

21.13 Derive the relation (21.87) between the differential scattering cross section and the scattering amplitude in box normalization.

21.14 Calculate the differential scattering cross section $d\sigma_{\mathbf{0};\boldsymbol{q},\alpha\to\boldsymbol{k}';\boldsymbol{q}'}/d\Omega$ for electron-photon scattering with polarized initial photons, i.e. sum over the polarizations of the scattered photons but do not average over the initial polarization.

21.15 Show that the differential scattering cross sections (21.104,21.106) for Compton scattering can also be written in the form

$$\begin{aligned} d\sigma_{\mathbf{0};\boldsymbol{q},\alpha\to\boldsymbol{k}';\boldsymbol{q}',\alpha'} &= d^3\boldsymbol{k}'d^3\boldsymbol{q}'\frac{\alpha^2\hbar^2\delta(k'+q'-k-q)}{4m|\boldsymbol{q}||\boldsymbol{q}'|E(\boldsymbol{k}')} \\ &\quad\times\left(4(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))^2 + \frac{|\boldsymbol{q}'|}{|\boldsymbol{q}|} + \frac{|\boldsymbol{q}|}{|\boldsymbol{q}'|} - 2\right), \qquad (21.118) \\ \frac{d\sigma_{\mathbf{0};\boldsymbol{q},\alpha\to\boldsymbol{q}-\boldsymbol{q}';\boldsymbol{q}',\alpha'}}{d\Omega} &= \left(\frac{\alpha\hbar|\boldsymbol{q}'|}{2mc|\boldsymbol{q}|}\right)^2\left(4(\boldsymbol{\epsilon}_\alpha(\boldsymbol{q})\cdot\boldsymbol{\epsilon}_{\alpha'}(\boldsymbol{q}'))^2 + \frac{|\boldsymbol{q}'|}{|\boldsymbol{q}|} + \frac{|\boldsymbol{q}|}{|\boldsymbol{q}'|} - 2\right). \end{aligned}$$

21.16 Calculate the kinetic energy imparted on the recoiling electron in Compton scattering as a function of $|\boldsymbol{q}|$ and θ.

Appendix A: Lagrangian Mechanics

Lagrangian mechanics is not only a very beautiful and powerful formulation of mechanics, but it is also the basis for a deeper understanding of all fundamental interactions in physics. All fundamental equations of motion in physics are encoded in Lagrangian field theory, which is a generalization of Lagrangian mechanics for fields. Furthermore, the connection between symmetries and conservation laws of physical systems is best explored in the framework of the Lagrangian formulation of dynamics, and we also need Lagrangian field theory as a basis for field quantization.

Suppose we consider a particle with coordinates $\boldsymbol{x}(t)$ moving in a potential $V(\boldsymbol{x})$. Then Newton's equation of motion

$$m\ddot{\boldsymbol{x}} = -\boldsymbol{\nabla} V(\boldsymbol{x})$$

is equivalent to the following statement (Hamilton's principle, 1834): The action integral

$$S[\boldsymbol{x}] = \int_{t_0}^{t_1} dt\, L(\boldsymbol{x}, \dot{\boldsymbol{x}}) = \int_{t_0}^{t_1} dt \left(\frac{m}{2}\dot{\boldsymbol{x}}^2 - V(\boldsymbol{x})\right)$$

is in first order stationary under arbitrary perturbations $\boldsymbol{x}(t) \to \boldsymbol{x}(t) + \delta\boldsymbol{x}(t)$ of the path of the particle between fixed endpoints $\boldsymbol{x}(t_0)$ and $\boldsymbol{x}(t_1)$ (i.e. the perturbation is only restricted by the requirement of fixed endpoints: $\delta\boldsymbol{x}(t_0) = 0$ and $\delta\boldsymbol{x}(t_1) = 0$). This is demonstrated by straightforward calculation of the first order variation of S,

$$\begin{aligned}\delta S[\boldsymbol{x}] &= S[\boldsymbol{x} + \delta\boldsymbol{x}] - S[\boldsymbol{x}] = \int_{t_0}^{t_1} dt\, [m\dot{\boldsymbol{x}} \cdot \delta\dot{\boldsymbol{x}} - \delta\boldsymbol{x} \cdot \boldsymbol{\nabla} V(\boldsymbol{x})] \\ &= -\int_{t_0}^{t_1} dt\, \delta\boldsymbol{x} \cdot (m\ddot{\boldsymbol{x}} + \boldsymbol{\nabla} V(\boldsymbol{x}))\,. \qquad \text{(A.1)}\end{aligned}$$

Partial integration and $\delta\boldsymbol{x}(t_0) = 0$, $\delta\boldsymbol{x}(t_1) = 0$ were used in the last step. Equation (A.1) tells us that $\delta S[\boldsymbol{x}] = 0$ holds for arbitrary path variation with fixed endpoints if and only if the path $\boldsymbol{x}(t)$ satisfies Newton's equations,

$$m\ddot{\boldsymbol{x}} + \boldsymbol{\nabla} V(\boldsymbol{x}) = 0.$$

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This generalizes to arbitrary numbers of particles ($\boldsymbol{x}(t) \to \boldsymbol{x}_I(t)$, $1 \leq I \leq N$), and to the case that the motion of the particles is restricted through constraints, like e.g. a particle that can only move on a sphere[11]. In the case of constraints one substitutes generalized coordinates $q_i(t)$ which correspond to the actual degrees of freedom of the particle or system of particles (e.g. polar angles for the particle on the sphere), and one ends up with an action integral of the form

$$S[q] = \int_{t_0}^{t_1} dt\, L(q, \dot{q}).$$

The function $L(q, \dot{q})$ is the *Lagrange function* of the mechanical system with generalized coordinates $q_i(t)$, and a shorthand notation is used for a mechanical system with N degrees of freedom,

$$(q, \dot{q}) = (q_1(t), q_2(t), \ldots, q_N(t), \dot{q}_1(t), \dot{q}_2(t), \ldots, \dot{q}_N(t)).$$

First order variation of the action with fixed endpoints (i.e. $\delta q(t_0) = 0$, $\delta q(t_1) = 0$) yields after partial integration

$$\begin{aligned} \delta S[q] = S[q + \delta q] - S[q] &= \int_{t_0}^{t_1} dt \left(\sum_i \delta q_i \frac{\partial L}{\partial q_i} + \sum_i \delta \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} \right) \\ &= \int_{t_0}^{t_1} dt \sum_i \delta q_i \left(\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} \right), \end{aligned} \tag{A.2}$$

where again fixation of the endpoints was used.
$\delta S[q] = 0$ for arbitrary path variation $q_i(t) \to q_i(t) + \delta q_i(t)$ with fixed endpoints then immediately tells us the equations of motion in terms of the generalized coordinates,

$$\frac{\partial L}{\partial q_i} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = 0. \tag{A.3}$$

These equations of motion are called Lagrange equations of the second kind or Euler-Lagrange equations or simply Lagrange equations. The quantity

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

is denoted as the *conjugate momentum* to the coordinate q_i.
The conjugate momentum is conserved if the Lagrange function depends only on the generalized velocity component $\dot{q}_i$ but not on q_i, $dp_i/dt = 0$.
Furthermore, if the Lagrange function does not explicity depend on time, we have

$$\frac{dL}{dt} = p_i \ddot{q}_i + \frac{\partial L}{\partial q_i} \dot{q}_i.$$

[11] And it also applies to relativistic particles, see Appendix B.

The Euler-Lagrange equation then implies that the Hamilton function

$$H = p_i \dot{q}_i - L$$

is conserved, $dH/dt = 0$.
For a simple example, consider a particle of mass m in a gravitational field $\boldsymbol{g} = -g\boldsymbol{e}_z$. The particle is constrained so that it can only move on a sphere of radius r. An example of generalized coordinates are angles ϑ, φ on the sphere, and the Cartesian coordinates $\{X, Y, Z\}$ of the particle are related to the generalized coordinates through

$$\begin{aligned} X(t) &= r \sin\vartheta(t) \cdot \cos\varphi(t), \\ Y(t) &= r \sin\vartheta(t) \cdot \sin\varphi(t), \\ Z(t) &= r \cos\vartheta(t). \end{aligned}$$

The kinetic energy of the particle can be expressed in terms of the generalized coordinates,

$$K = \frac{m}{2}\dot{\boldsymbol{r}}^2 = \frac{m}{2}\left(\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2\right) = \frac{m}{2} r^2 \left(\dot{\vartheta}^2 + \dot{\varphi}^2 \sin^2\vartheta\right),$$

and the potential energy is

$$V = mgZ = mgr\cos\vartheta.$$

This yields the Lagrange function in the generalized coordinates,

$$L = \frac{m}{2}\dot{\boldsymbol{r}}^2 - mgZ = \frac{m}{2} r^2 \left(\dot{\vartheta}^2 + \dot{\varphi}^2 \sin^2\vartheta\right) - mgr\cos\vartheta,$$

and the Euler-Lagrange equations yield the equations of motion of the particle,

$$\ddot{\vartheta} = \dot{\varphi}^2 \sin\vartheta\cos\vartheta + \frac{g}{r}\sin\vartheta, \tag{A.4}$$

$$\frac{d}{dt}\left(\dot{\varphi}\sin^2\vartheta\right) = 0. \tag{A.5}$$

The conjugate momenta

$$p_\vartheta = \frac{\partial L}{\partial \dot{\vartheta}} = mr^2\dot{\vartheta}$$

and

$$p_\varphi = \frac{\partial L}{\partial \dot{\varphi}} = mr^2\dot{\varphi}\sin^2\vartheta$$

are just the angular momenta for rotation in ϑ or φ direction. The Hamilton function is the conserved energy

$$H = p_\vartheta\dot{\vartheta} + p_\varphi\dot{\varphi} - L = \frac{p_\vartheta^2}{2mr^2} + \frac{p_\varphi^2}{2mr^2\sin^2\vartheta} + mgr\cos\vartheta = K + U.$$

The immediately apparent advantage of this formalism is that it directly yields the correct equations of motion (A.4,A.5) for the system without ever having to worry about finding the force that keeps the particle on the sphere. Beyond that the formalism also provides a systematic way to identify conservation laws in mechanical systems, and if one actually wants to know the force that keeps the particle on the sphere (which is actually trivial here, but more complicated e.g. for a system of two particles which have to maintain constant distance), a simple extension of the formalism to the Lagrange equations of the first kind can yield that, too.
The Lagrange function is not simply the difference between kinetic and potential energy if the forces are velocity dependent. This is the case for the Lorentz force. The Lagrange function for a non-relativistic charged particle in electromagnetic fields is

$$L = \frac{m}{2}\dot{\boldsymbol{x}}^2 + q\dot{\boldsymbol{x}} \cdot \boldsymbol{A} - q\Phi.$$

This yields the correct Lorentz force law $m\ddot{\boldsymbol{x}} = q(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B})$ for the particle, cf. Section 15.1. The relativistic versions of the Lagrange finction for the particle can be found in equations (B.24,B.25).

Direct derivation of the Euler-Lagrange equations for the generalized coordinates q_a from Newton's equation in Cartesian coordinates

We can derive the Euler-Lagrange equations for the generalized coordinates of a constrained N-particle system directly from Newton's equations. This works in the following way:
Suppose we have N particles with coordinates ${x_i}^j$, $1 \leq i \leq N$, $1 \leq j \leq 3$, moving in a potential $V(\boldsymbol{x}_{1\ldots N})$. The Newton equations

$$\frac{d}{dt}(m_i \dot{{x_i}}^j) + \frac{\partial}{\partial {x_i}^j} V(\boldsymbol{x}_{1\ldots N}) = 0$$

can be written as

$$\Big(\frac{d}{dt}\frac{\partial}{\partial \dot{{x_i}}^j} - \frac{\partial}{\partial {x_i}^j}\Big)\Big(\frac{1}{2}\sum_k m_k \dot{\boldsymbol{x}}_k^2 - V(\boldsymbol{x}_{1\ldots N})\Big) = 0, \tag{A.6}$$

or equivalently

$$\Big(\frac{d}{dt}\frac{\partial}{\partial \dot{{x_i}}^j} - \frac{\partial}{\partial {x_i}^j}\Big) L(\boldsymbol{x}_{1\ldots N}, \dot{\boldsymbol{x}}_{1\ldots N}) = 0, \tag{A.7}$$

with the Lagrange function

$$L(\boldsymbol{x}_{1\ldots N}, \dot{\boldsymbol{x}}_{1\ldots N}) = \frac{1}{2}\sum_i m_i \dot{\boldsymbol{x}}_i^2 - V(\boldsymbol{x}_{1\ldots N}). \tag{A.8}$$

If there are C holonomic constraints on the motion of the N-particle system, we can describe its trajectories through $3N - C$ generalized coordinates q_a, $1 \le a \le 3N - C$:

$$x_i{}^j = x_i{}^j(q, t). \tag{A.9}$$

Note that in general $x_i{}^j(q, t)$ will implicitly depend on time t through the time dependence of the generalized coordinates $q_a(t)$, but it may also explicitly depend on t because there may be a time dependence in the C constraints. (A simple example for the latter would e.g. be a particle that is bound to a sphere with time-dependent radius $R(t)$, where $R(t)$ is a given time-dependent function.)
The velocity components of the system are

$$\dot{x}_i{}^j = \frac{dx_i{}^j}{dt} = \sum_a \dot{q}_a \frac{\partial x_i{}^j}{\partial q_a} + \frac{\partial x_i{}^j}{\partial t}. \tag{A.10}$$

This implies in particular the equations

$$\frac{\partial \dot{x}_i{}^j}{\partial \dot{q}_a} = \frac{\partial x_i{}^j}{\partial q_a} \tag{A.11}$$

and

$$\frac{\partial \dot{x}_i{}^j}{\partial q_a} = \sum_b \dot{q}_b \frac{\partial^2 x_i{}^j}{\partial q_a \partial q_b} + \frac{\partial^2 x_i{}^j}{\partial t \partial q_a}. \tag{A.12}$$

Substitution of (A.11) into (A.12) yields

$$\frac{\partial \dot{x}_i{}^j}{\partial q_a} = \sum_b \dot{q}_b \frac{\partial^2 \dot{x}_i{}^j}{\partial q_b \partial \dot{q}_a} + \frac{\partial^2 \dot{x}_i{}^j}{\partial t \partial \dot{q}_a}. \tag{A.13}$$

Equation (A.11) also yields

$$\frac{\partial^2 \dot{x}_i{}^j}{\partial \dot{q}_a \partial \dot{q}_b} = 0,$$

and this implies with (A.13)

$$\frac{d}{dt}\frac{\partial \dot{x}_i{}^j}{\partial \dot{q}_a} = \sum_b \dot{q}_b \frac{\partial^2 \dot{x}_i{}^j}{\partial q_b \partial \dot{q}_a} + \frac{\partial^2 \dot{x}_i{}^j}{\partial t \partial \dot{q}_a} = \frac{\partial \dot{x}_i{}^j}{\partial q_a}. \tag{A.14}$$

With these preliminaries we can now look at the following linear combinations of the Newton equations (A.7):

$$\sum_{i,j} \frac{\partial x_i{}^j}{\partial q_a} \cdot \left(\frac{d}{dt}\frac{\partial L}{\partial \dot{x}_i{}^j} - \frac{\partial L}{\partial x_i{}^j} \right) = 0.$$

Insertion of equations (A.11,A.14) yields

$$\sum_{i,j}\Big[\frac{\partial \dot{x}_i{}^j}{\partial \dot{q}_a}\frac{d}{dt}\frac{\partial L}{\partial \dot{x}_i{}^j}-\frac{\partial x_i{}^j}{\partial q_a}\frac{\partial L}{\partial x_i{}^j}+\Big(\frac{d}{dt}\frac{\partial \dot{x}_i{}^j}{\partial \dot{q}_a}-\frac{\partial \dot{x}_i{}^j}{\partial q_a}\Big)\frac{\partial L}{\partial \dot{x}_i{}^j}\Big]=0,$$

or after combining terms:

$$\frac{d}{dt}\sum_{i,j}\Big(\frac{\partial \dot{x}_i{}^j}{\partial \dot{q}_a}\frac{\partial L}{\partial \dot{x}_i{}^j}\Big)-\frac{\partial L}{\partial q_a}=0. \tag{A.15}$$

However, the coordinates $x_i{}^j$ are independent of the generalized velocities $\dot{q}_a$, and therefore equation (A.15) is just the Lagrange equation (A.3):

$$\frac{d}{dt}\frac{\partial L(q,\dot{q})}{\partial \dot{q}_a}-\frac{\partial L(q,\dot{q})}{\partial q_a}=0. \tag{A.16}$$

Appendix B: The Covariant Formulation of Electrodynamics

Electrodynamics is a relativistic field theory for every frequency or energy of electromagnetic waves because photons are massless. Understanding of electromagnetism and of photon-matter interactions therefore requires an understanding of special relativity. Furthermore, we also want to understand the quantum mechanics of relativistic electrons and other relativistic particles, and the covariant formulation of electrodynamics is also very helpful as a preparation for relativistic wave equations like the Klein-Gordon and Dirac equations.

Lorentz transformations

The scientific community faced several puzzling problems around 1900. Some of these problems led to the development of quantum mechanics, but two of the problems motivated Einstein's Special Theory of Relativity:

• In 1881 and 1887 Michelson had demonstrated that light from a terrestrial light source always moves with the same speed c in each direction, irrespective of Earth's motion.

• The basic equation of Newtonian mechanics, $\boldsymbol{F} = d(m\boldsymbol{u})/dt$, is invariant under Galilei transformations of the coordinates:

$$t' = t, \quad \boldsymbol{x}' = \boldsymbol{x} - \boldsymbol{v}t. \tag{B.1}$$

Therefore any two observers who use coordinates related through a Galilei transformation are physically equivalent in Newtonian mechanics.

However, in 1887 (at the latest) it was realized that Galilei transformations do not leave Maxwell's equations invariant, i.e. if Maxwell's equations describe electromagnetic phenomena for one observer, they would not hold for another observer moving with constant velocity $\boldsymbol{v}$ relative to the first observer (because it was assumed that the coordinates of these two observers are related through the Galilei transformation (B.1)). Instead, Voigt (1887) and Lorentz (1892-1904) realized that Maxwell's equations would hold for the two observers if their coordinates would be related e.g. through a transformation of the form

$$ct' = \frac{ct - (v/c)x}{\sqrt{1-(v^2/c^2)}}, \quad x' = \frac{x - vt}{\sqrt{1-(v^2/c^2)}}, \quad y' = y, \quad z' = z, \tag{B.2}$$

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and they also realized that coordinate transformations of this kind imply that light would move with the same speed c in both coordinate systems,

$$\Delta x^2 + \Delta y^2 + \Delta z^2 - c^2\Delta t^2 = \Delta x'^2 + \Delta y'^2 + \Delta z'^2 - c^2\Delta t'^2. \tag{B.3}$$

Voigt was interested in the most general symmetry transformation of the wave equations for electromagnetic fields, while Lorentz tried to explain the results of the Michelson experiment.

In 1905 Einstein took the bold step to propose that then the coordinates measured by two observers with constant relative speed $\boldsymbol{v}$ must be described by transformations like (B.2), but *not* by Galilei transformations[12]. This was a radical step, because it implies that two observers with non-vanishing relative speed assign different time coordinates to one and the same event, and they also have different notions of simultaneity of events. The same statement in another formulation: Two different observers with non-vanishing relative speed slice the four-dimensional universe differently into three-dimensional regions of simultaneity, or into three-dimensional universes. Einstein abandoned the common prejudice that everybody always assigns the same time coordinate to one and the same event. Time is not universal. The speed of light in vacuum is universal.

In the following we use the abbreviations

$$\beta = \frac{v}{c}, \quad \gamma = \frac{1}{\sqrt{1-\beta^2}}.$$

The transformation (B.2) and its inversion then read

$$ct' = \gamma(ct - \beta x), \quad x' = \gamma(x - \beta ct), \quad y' = y, \quad z' = z, \tag{B.4}$$

$$ct = \gamma(ct' + \beta x'), \quad x = \gamma(x' + \beta ct'). \tag{B.5}$$

The spatial origin $x' = y' = z' = 0$ of the (ct', x', y', z') system satisfies $x = \beta ct = vt$ (use $x' = 0$ in $x' = \gamma(x - \beta ct)$), and therefore moves with velocity $v\boldsymbol{e}_x$ relative to the (ct, x, y, z) system. In the same way one finds that the spatial origin of the (ct, x, y, z) system moves with velocity $-v\boldsymbol{e}'_x$ through the (ct', x', y', z') system. Therefore this is the special Lorentz transformation between two coordinate frames with a relative motion with speed v in x-direction as seen from the unprimed frame, or in $(-x')$-direction as seen from the primed frame.

Equation (B.2) tells us that for motion in a certain direction (x-direction in (B.2)), the coordinate in that direction is affected non-trivially by the tranformation, while any orthogonal coordinate does not change its value. This immediatey allows for a generalization of (B.2) in the case that the relative velocity $\boldsymbol{v}$ points in an arbitrary direction.

[12]This idea was also enunciated by Poincaré in 1904, but Einstein went beyond the statement of the idea and also worked out the consequences.

It is convenient to introduce a rescaled velocity vector $\boldsymbol{\beta} = \boldsymbol{v}/c$ and the corresponding unit vector $\hat{\boldsymbol{\beta}} = \boldsymbol{\beta}/\beta = \boldsymbol{v}/v$. The (3×3)-matrix $\hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T$ projects any vector $\boldsymbol{x}$ onto its component parallel to $\boldsymbol{\beta}$,

$$\boldsymbol{x}_{\parallel\boldsymbol{\beta}} = \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T \cdot \boldsymbol{x},$$

while the component orthogonal to $\boldsymbol{\beta}$ is

$$\boldsymbol{x}_{\perp\boldsymbol{\beta}} = \boldsymbol{x} - \boldsymbol{x}_{\parallel\boldsymbol{\beta}} = (\underline{1} - \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T) \cdot \boldsymbol{x}.$$

From the form of the special Lorentz transformation (B.2) we know that the coordinate $|\boldsymbol{x}_{\parallel\boldsymbol{\beta}}|$ parallel to $\boldsymbol{v}$ will be rescaled by a factor

$$\gamma = \frac{1}{\sqrt{1 - (v^2/c^2)}} = \frac{1}{\sqrt{1 - \beta^2}},$$

and be shifted by an amount $-\gamma v t = -\gamma\beta ct$. Similarly, the time coordinate ct will be rescaled by the factor γ and be shifted by an amount $-\gamma\beta|\boldsymbol{x}_{\parallel\boldsymbol{\beta}}|$. Finally, nothing will happen to the transverse component $\boldsymbol{x}_{\perp\boldsymbol{\beta}}$. We can collect these observations in a (4×4)-matrix equation relating the two four-dimensional coordinate vectors,

$$\begin{pmatrix} ct' \\ \boldsymbol{x}' \end{pmatrix} = \begin{pmatrix} \gamma & -\gamma\boldsymbol{\beta}^T \\ -\gamma\boldsymbol{\beta} & \underline{1} - \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T + \gamma\hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T \end{pmatrix} \cdot \begin{pmatrix} ct \\ \boldsymbol{x} \end{pmatrix}$$

This is the general Lorentz transformation between two observers if the spatial sections of their coordinate frames were coincident at $t = 0$. The most general transformation of this kind also allows for constant shifts of the coordinates and for a rotation of the spatial axes,

$$\begin{pmatrix} ct' \\ \boldsymbol{x}' \end{pmatrix} = \begin{pmatrix} \gamma & -\gamma\boldsymbol{\beta}^T \\ -\gamma\boldsymbol{\beta} & \underline{1} - \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T + \gamma\hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T \end{pmatrix} \cdot \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \underline{R} \end{pmatrix} \cdot \begin{pmatrix} ct - cT \\ \boldsymbol{x} - \boldsymbol{X} \end{pmatrix}, \tag{B.6}$$

where $\underline{R}$ is a 3×3 rotation matrix. Without the coordinate shifts this is the most general orthochronous Lorentz transformation, where *orthochronous* refers to the fact that we did not include a possible reversal of the time axis. With the coordinate shifts included, (B.6) is denoted as an inhomogeneous Lorentz transformation or a Poincaré transformation. The Poincaré transformations (B.6) and the subset of Lorentz transformations ($T = 0$, $\boldsymbol{X} = \mathbf{0}$) form the *Poincaré group* and the *Lorentz group*, respectively. The Lorentz group is apparently a subgroup of the Poincaré group, and the rotation group is a subgroup of the Lorentz group.

In four-dimensional notation the 4-vector of coordinates is $x^\mu = (ct, \boldsymbol{x})$, and the 4-vector short hand for equation (B.6) is

$$x'^\mu = \Lambda^\mu{}_\nu (x^\nu - X^\nu). \tag{B.7}$$

where the (4×4) transformation matrix Λ is

$$\Lambda = \{\Lambda^{\mu}{}_{\nu}\} = \begin{pmatrix} \gamma & -\gamma\boldsymbol{\beta}^T \\ -\gamma\boldsymbol{\beta} & \underline{1} - \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T + \gamma\hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T \end{pmatrix} \cdot \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \underline{R} \end{pmatrix}. \tag{B.8}$$

A homogeneous Lorentz transformation of this form is denoted as a *proper orthochronous Lorentz transformation* if we also exclude inversions of an odd number of spatial axis, which is equivalent to the requirement $\det \underline{R} = 1$.
We will see below that it plays a role where we attach the indices for the explicit numerical representation of the matrix Λ in terms of matrix elements. Usually, if a matrix is given for Λ without explicitly defining index positions, the default convention is that it refers to a superscript row index and a subscript column index, as above, $\Lambda = \{\Lambda^{\mu}{}_{\nu}\}$. This is important, because as soon as a boost is involved (i.e. $\boldsymbol{\beta} \neq \mathbf{0}$), we will find that e.g.

$$\Lambda^{\mu}{}_{\nu}(\boldsymbol{\beta}) = \Lambda_{\nu}{}^{\mu}(-\boldsymbol{\beta}) \neq \Lambda_{\nu}{}^{\mu}(\boldsymbol{\beta}).$$

The transformation equation (B.6) is the general solution to the following problem: Find the most general coordinate transformation $\{ct, \boldsymbol{x}\} = \{ct, x, y, z\} \to \{ct', \boldsymbol{x}'\} = \{ct', x', y', z'\}$ which leaves the expression $\Delta\boldsymbol{x}^2 - c^2\Delta t^2$ invariant, i.e. such that for arbitrary coordinate differentials $c\Delta t, \Delta\boldsymbol{x}$ we have

$$\Delta\boldsymbol{x}^2 - c^2\Delta t^2 = \Delta\boldsymbol{x}'^2 - c^2\Delta t'^2. \tag{B.9}$$

This equation implies in particular that if one of our observers sees a light wave moving at speed c, then this light wave will also move with speed c for the second observer,

$$\Delta\boldsymbol{x}^2 - c^2\Delta t^2 = 0 \;\Leftrightarrow\; \Delta\boldsymbol{x}'^2 - c^2\Delta t'^2 = 0.$$

In fact it suffices to require *only* that anything moving with speed c will also have speed c in the new coordinates, and that the spatial coordinates are Cartesian in both frames. Up to rescalings of the coordinates the most general coordinate transformation is then the general inhomogeneous Lorentz transformation (B.6).
Any constant offset X^{μ} between coordinate systems vanishes for differences of coordinates. Equation (B.7) therefore implies the following equation for Lorentz transformation of coordinate differentials,

$$dx'^{\mu} = \Lambda^{\mu}{}_{\alpha} dx^{\alpha}. \tag{B.10}$$

The condition (B.9),

$$d\boldsymbol{x}^2 - c^2 dt^2 = d\boldsymbol{x}'^2 - c^2 dt'^2$$

can also be written as

$$\eta_{\mu\nu} dx'^{\mu} dx'^{\nu} = \eta_{\alpha\beta} dx^{\alpha} dx^{\beta} \tag{B.11}$$

with the special (4×4)-matrix ($\underline{1}$ is the 3×3 unit matrix)

$$\eta_{\mu\nu} = \begin{pmatrix} -1 & \mathbf{0}^T \\ \mathbf{0} & \underline{1} \end{pmatrix},$$

Equation (B.9) also implies

$$\eta_{\mu\nu} dx'^{\mu} dy'^{\nu} = \eta_{\alpha\beta} dx^{\alpha} dy^{\beta}$$

for any pair of Lorentz transformed 4-vectors dx and dy (simply insert the 4-vector $dx + dy$ into (B.11)). This implies that Lorentz transformations leave the *Minkowski metric* $\eta_{\mu\nu}$ invariant:

$$\eta_{\mu\nu} \Lambda^{\mu}{}_{\alpha} \Lambda^{\nu}{}_{\beta} = \eta_{\alpha\beta}. \tag{B.12}$$

If we multiply this equation with the components $\eta^{\beta\gamma}$ of the inverse Minkowski tensor, we find

$$\eta_{\mu\nu} \Lambda^{\mu}{}_{\alpha} \Lambda^{\nu}{}_{\beta} \eta^{\beta\gamma} = \delta_{\alpha}{}^{\gamma} \equiv \eta_{\alpha}{}^{\gamma}.$$

This tells us a relation between the (4×4)-matrix Λ with "pulled indices" and its inverse Λ^{-1}:

$$\Lambda_{\mu}{}^{\gamma} \equiv \eta_{\mu\nu} \Lambda^{\nu}{}_{\beta} \eta^{\beta\gamma} = (\Lambda^{-1})^{\gamma}{}_{\mu}. \tag{B.13}$$

Explicitly, if

$$\{\Lambda^{\mu}{}_{\nu}\} = \begin{pmatrix} \gamma & -\gamma \boldsymbol{\beta}^T \\ -\gamma \boldsymbol{\beta} & \underline{1} - \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T + \gamma \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T \end{pmatrix} \cdot \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \underline{R} \end{pmatrix}$$

then

$$\{\Lambda_{\mu}{}^{\nu}\} \equiv \{\eta_{\mu\rho} \Lambda^{\rho}{}_{\sigma} \eta^{\sigma\nu}\} = \begin{pmatrix} \gamma & \gamma \boldsymbol{\beta}^T \\ \gamma \boldsymbol{\beta} & \underline{1} - \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T + \gamma \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T \end{pmatrix} \cdot \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \underline{R} \end{pmatrix}.$$

We can also "pull" or "draw" indices on 4-vectors, e.g. $dx_{\alpha} \equiv \eta_{\alpha\beta} dx^{\beta} = (-c dt, d\boldsymbol{x})$. Let us figure out how this 4-vector transforms under the Lorentz transformation (B.10):

$$dx'_{\mu} = \eta_{\mu\nu} dx'^{\nu} = \eta_{\mu\nu} \Lambda^{\nu}{}_{\alpha} dx^{\alpha} = \eta_{\mu\nu} \Lambda^{\nu}{}_{\alpha} \eta^{\alpha\beta} dx_{\beta} = \Lambda_{\mu}{}^{\beta} dx_{\beta} = dx_{\beta} (\Lambda^{-1})^{\beta}{}_{\mu}.$$

4-vectors with this kind of transformation behavior are denoted as *covariant 4-vectors*, while dx^{μ} is an example of a *contravariant 4-vector*. Another example of a covariant 4-vector is the vector of partial derivatives

$$\partial_{\mu} \equiv \frac{\partial}{\partial x^{\mu}} = \left(\frac{1}{c} \frac{\partial}{\partial t}, \boldsymbol{\nabla} \right).$$

We can check that this is really a covariant 4-vector by calculating how it transforms under Lorentz transformations. According to the chain rule of differentiation we find

$$\partial'_\mu \equiv \frac{\partial}{\partial x'^\mu} = \frac{\partial x^\alpha}{\partial x'^\mu}\frac{\partial}{\partial x^\alpha}.$$

However, we have

$$dx^\alpha = (\Lambda^{-1})^\alpha{}_\nu dx'^\nu \quad \Rightarrow \quad \frac{\partial x^\alpha}{\partial x'^\mu} = (\Lambda^{-1})^\alpha{}_\mu$$

and therefore

$$\partial'_\mu = (\Lambda^{-1})^\alpha{}_\mu \partial_\alpha = \Lambda_\mu{}^\alpha \partial_\alpha.$$

Pairs of co- and contravariant indices do not transform if they are summed over. Assume e.g. that $F^{\alpha\beta}$ are the components of a 4×4 matrix which transform according to

$$F^{\alpha\beta} \to F'^{\mu\nu} = \Lambda^\mu{}_\alpha \Lambda^\nu{}_\beta F^{\alpha\beta}.$$

The combination $\partial_\alpha F^{\alpha\beta}$ then transforms under Lorentz transformations according to

$$\partial'_\mu F'^{\mu\nu} = \Lambda_\mu{}^\alpha \partial_\alpha \Lambda^\mu{}_\beta \Lambda^\nu{}_\gamma F^{\beta\gamma} = \Lambda^\nu{}_\gamma \eta^\alpha{}_\beta \partial_\alpha F^{\beta\gamma} = \Lambda^\nu{}_\gamma \partial_\alpha F^{\alpha\gamma},$$

i.e. the summed index pair does not contribute to the transformation. Only "free" indices (i.e. indices which are not paired and summed from 0 to 3) transform under Lorentz transformations.

The manifestly covariant formulation of electrodynamics

Electrodynamics is a Lorentz invariant theory, i.e. all equations have the same form in all coordinate systems which are related by Poincaré transformations. However, this property is hardly recognizable if one looks at Maxwell's equations in traditional notation,

$$\boldsymbol{\nabla} \cdot \boldsymbol{E} = \frac{1}{\epsilon_0}\varrho, \quad \boldsymbol{\nabla} \times \boldsymbol{E} + \frac{\partial}{\partial t}\boldsymbol{B} = \boldsymbol{0},$$

$$\boldsymbol{\nabla} \cdot \boldsymbol{B} = 0, \quad \boldsymbol{\nabla} \times \boldsymbol{B} - \frac{1}{c^2}\frac{\partial}{\partial t}\boldsymbol{E} = \mu_0 \boldsymbol{j}.$$

"Lorentz invariance" seems far from obvious: How, e.g. would the electric and magnetic fields transform under a Lorentz transformation of the coordinates? Apparently we seem to have three 3-dimensional vectors and one scalar in the equations. We can combine the current density $\boldsymbol{j}$ and the charge density ϱ into a current 4-vector

$$j^\nu = (\varrho c, \boldsymbol{j}).$$

For the field strengths it helps to recall that the homogeneous Maxwell's equations are solved through potentials Φ, $\boldsymbol{A}$,

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}, \quad \boldsymbol{E} = -\frac{\partial}{\partial t}\boldsymbol{A} - \boldsymbol{\nabla}\Phi.$$

If one combines the potentials into a 4-vector

$$A_\mu = (-\Phi/c, \boldsymbol{A}),$$

it is possible to realize that the electromagnetic field strengths E_i, B_i are related to antisymmetric combinations of the 4-vectors ∂_μ, A_ν,

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu = \begin{pmatrix} 0 & -E_1/c & -E_2/c & -E_3/c \\ E_1/c & 0 & B_3 & -B_2 \\ E_2/c & -B_3 & 0 & B_1 \\ E_3/c & B_2 & -B_1 & 0 \end{pmatrix}.$$

This electromagnetic field strength tensor $\underline{F}$ was introduced by Minkowski in 1907[13]. $F_{\mu\nu}$ are its covariant components. The contravariant components of $\underline{F}$ are

$$F^{\mu\nu} = \eta^{\mu\alpha}\eta^{\nu\beta}F_{\alpha\beta} = \partial^\mu A^\nu - \partial^\nu A^\mu = \begin{pmatrix} 0 & E_1/c & E_2/c & E_3/c \\ -E_1/c & 0 & B_3 & -B_2 \\ -E_2/c & -B_3 & 0 & B_1 \\ -E_3/c & B_2 & -B_1 & 0 \end{pmatrix}.$$

From this one can easily read off the transformation behavior of the fields under Lorentz transformations,

$$x^\mu \to x'^\mu = \Lambda^\mu{}_\alpha x^\alpha,$$

$$\partial_\mu \to \partial'_\mu = \Lambda_\mu{}^\alpha \partial_\alpha,$$
$$A_\mu(x) \to A'_\mu(x') = \Lambda_\mu{}^\alpha A_\alpha(x)$$

$$\begin{aligned} F_{\mu\nu}(x) \to F'_{\mu\nu}(x') &= \partial'_\mu A'_\nu(x') - \partial'_\nu A'_\mu(x') = \Lambda_\mu{}^\alpha \Lambda_\nu{}^\beta (\partial_\alpha A_\beta(x) - \partial_\beta A_\alpha(x)) \\ &= \Lambda_\mu{}^\alpha \Lambda_\nu{}^\beta F_{\alpha\beta}(x). \end{aligned}$$

Evaluation of $F'_{\mu\nu}(x')$ for a boost

$$\{\Lambda^\mu{}_\nu\} = \begin{pmatrix} \gamma & -\gamma\boldsymbol{\beta}^T \\ -\gamma\boldsymbol{\beta} & \underline{1} - \hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T + \gamma\hat{\boldsymbol{\beta}} \otimes \hat{\boldsymbol{\beta}}^T \end{pmatrix}$$

[13] H. Minkowski, Math. Ann. 68, 472 (1910).

yields with $\boldsymbol{\beta} = \boldsymbol{v}/c$

$$\begin{aligned}
\boldsymbol{E}'(\boldsymbol{x}', t') &= \gamma\Big(\boldsymbol{E}(\boldsymbol{x}, t) + \boldsymbol{v} \times \boldsymbol{B}(\boldsymbol{x}, t)\Big) - (\gamma - 1)\hat{\boldsymbol{\beta}}\Big(\hat{\boldsymbol{\beta}} \cdot \boldsymbol{E}(\boldsymbol{x}, t)\Big) \\
&= \gamma\Big(\boldsymbol{E}(\boldsymbol{x}, t) + \boldsymbol{v} \times \boldsymbol{B}(\boldsymbol{x}, t)\Big) - \frac{\gamma^2}{(\gamma + 1)c^2}\boldsymbol{v}\Big(\boldsymbol{v} \cdot \boldsymbol{E}(\boldsymbol{x}, t)\Big), \\
\boldsymbol{B}'(\boldsymbol{x}', t') &= \gamma\left(\boldsymbol{B}(\boldsymbol{x}, t) - \frac{1}{c^2}\boldsymbol{v} \times \boldsymbol{E}(\boldsymbol{x}, t)\right) - (\gamma - 1)\hat{\boldsymbol{\beta}}\Big(\hat{\boldsymbol{\beta}} \cdot \boldsymbol{B}(\boldsymbol{x}, t)\Big) \\
&= \gamma\left(\boldsymbol{B}(\boldsymbol{x}, t) - \frac{1}{c^2}\boldsymbol{v} \times \boldsymbol{E}(\boldsymbol{x}, t)\right) - \frac{\gamma^2}{(\gamma + 1)c^2}\boldsymbol{v}\Big(\boldsymbol{v} \cdot \boldsymbol{B}(\boldsymbol{x}, t)\Big).
\end{aligned}$$

Electric and magnetic fields mix under Lorentz transformations, i.e. the distinction between electric and magnetic fields depends on the observer.
The equations

$$\partial_\mu F^{\mu\nu} = -\mu_0 j^\nu$$

are the inhomogeneous Maxwell's equations

$$\boldsymbol{\nabla} \cdot \boldsymbol{E} = \frac{1}{\epsilon_0}\varrho, \quad \boldsymbol{\nabla} \times \boldsymbol{B} - \frac{1}{c^2}\frac{\partial}{\partial t}\boldsymbol{E} = \mu_0 \boldsymbol{j},$$

while the identities (with the 4-dimensional ϵ-tensor, $\epsilon^{0123} = -1$)

$$\epsilon^{\kappa\lambda\mu\nu}\partial_\lambda F_{\mu\nu} = 2\epsilon^{\kappa\lambda\mu\nu}\partial_\lambda\partial_\mu A_\nu \equiv 0$$

are the homogeneous Maxwell's equations

$$\boldsymbol{\nabla} \cdot \boldsymbol{B} = 0, \quad \boldsymbol{\nabla} \times \boldsymbol{E} + \frac{\partial}{\partial t}\boldsymbol{B} = \boldsymbol{0}.$$

These identities can also written in terms of the dual field strength tensor

$$\tilde{F}^{\mu\nu} = \frac{1}{2}\epsilon^{\mu\nu\alpha\beta}F_{\alpha\beta} = \begin{pmatrix} 0 & -B_1 & -B_2 & -B_3 \\ B_1 & 0 & E_3/c & -E_2/c \\ B_2 & -E_3/c & 0 & E_1/c \\ B_3 & E_2/c & -E_1/c & 0 \end{pmatrix}$$

as

$$\partial_\mu \tilde{F}^{\mu\nu} = 0.$$

The gauge freedom $A_\mu(x) \to A'_\mu(x) = A_\mu(x) + \partial_\mu f(x)$ apparently leaves the field strength tensor $F_{\mu\nu}$ invariant. In conventional terms this is

$$\Phi'(x) = \Phi(x) - \dot{f}(x), \quad \boldsymbol{A}'(x) = \boldsymbol{A}(x) + \boldsymbol{\nabla} f(x).$$

We have written Maxwell's equations explicitly as equations between 4-vectors,

$$\partial_\mu F^{\mu\nu} = -\mu_0 j^\nu, \quad \partial_\mu \tilde{F}^{\mu\nu} = 0,$$

and this ensures that they hold in this form for every inertial observer. This is the *form invariance* (or simply "invariance") of Maxwell's equations under Lorentz transformations.
With the identification of the current 4-vector $j^\mu = (\varrho c, \boldsymbol{j})$, the local conservation law for charges can also be written in manifestly Lorentz invariant form,

$$\frac{\partial}{\partial t}\varrho + \boldsymbol{\nabla}\cdot\boldsymbol{j} = \partial_\mu j^\mu = 0.$$

Relativistic mechanics

In special relativity it is better to express everything in quantities which transform linearly with combinations of the matrices Λ and Λ^{-1}. As a consequence of the transformation law

$$dx'^\mu = \Lambda^\mu{}_\nu dx^\nu, \tag{B.14}$$

ordinary velocities $d\boldsymbol{x}/dt$ and accelerations $d^2\boldsymbol{x}/dt^2$ transform nonlinearly under Lorentz boosts, due to the transformation of the time coordinates in the denominators. Therefore it is convenient to substitute the physical velocities and accelerations with "proper" velocities and accelerations, which do not require division by a transforming time parameter t.
Suppose the x'-frame is the frame of a moving object. In its own frame the trajectory of the object is $\boldsymbol{x}' = 0$. However, we know that the Lorentz transformation (B.14) leaves the product $dx^\mu dx_\mu$ invariant,

$$dx'^\mu dx'_\mu = d\boldsymbol{x}'^2 - c^2 dt'^2 = dx^\mu dx_\mu = d\boldsymbol{x}^2 - c^2 dt^2.$$

Therefore we have in particular for the time $dt' \equiv d\tau$ measured by the moving object along its own path $\boldsymbol{x}' = 0$

$$d\tau^2 = dt^2 - \frac{1}{c^2}d\boldsymbol{x}^2 = \left(1 - \frac{v^2}{c^2}\right)dt^2,$$

i.e. up to a constant

$$\tau = \int dt\,\sqrt{1-(v^2/c^2)} = \int \frac{dt}{\gamma}.$$

This is an *invariant*, i.e. it has the same value for each observer. Every observer will measure their own specific time interval Δt between any two events happening to the moving object, but all observers agree on the same value

$$\Delta\tau = \int_0^{\Delta t} dt\,\sqrt{1-(v^2/c^2)}$$

which elapsed on a clock moving with the object.

The time $\Delta\tau$ measured by an object between any two events happening to the object is denoted as the *proper time* or *eigentime* of the object.
The definition of eigentime entails a corresponding definition of the *proper velocity* or *eigenvelocity* of an object in an observer's frame: Divide the change in the object's coordinates $d\boldsymbol{x}$ *in the observer's frame* by the time interval $d\tau$ elapsed *for the object itself* while it was moving by $d\boldsymbol{x}$:

$$\boldsymbol{U} = \frac{d\boldsymbol{x}}{d\tau} = \gamma\frac{d\boldsymbol{x}}{dt} = \gamma\boldsymbol{v}.$$

This is a hybrid construction in the sense that a set of coordinate intervals $d\boldsymbol{x}$ measured in the observer's frame is divided by a coordinate interval $d\tau$ measured in the object's frame[14].
The notion of proper velocity may seem a little artificial, but it is useful because it can be extended to a 4-vector using the fact that $\{dx^\mu\} = (dx^0, d\boldsymbol{x}) = (cdt, d\boldsymbol{x})$ is a 4-vector under Lorentz transformations. If we define

$$U^0 = \frac{dx^0}{d\tau} = \frac{cdt}{d\tau} = \gamma c,$$

then

$$U^\mu = dx^\mu/d\tau = (U^0, \boldsymbol{U}) = \gamma(c, \boldsymbol{v})$$

is a 4-vector which tranforms according to $U^\mu \to U'^\mu = \Lambda^\mu{}_\alpha U^\alpha$ under Lorentz transformations. This *4-velocity* vector satisfies

$$U^2 \equiv U^\mu U_\mu \equiv \eta_{\mu\nu}U^\mu U^\nu = \boldsymbol{U}^2 - (U^0)^2 = -c^2.$$

The conservation laws

$$\sum_i \boldsymbol{p}_i^{(in)} = \sum_i \boldsymbol{p}_i^{(out)}$$

$$\sum_i E_i^{(in)} = \sum_i E_i^{(out)}$$

for momentum and energy in a collision would not be preserved under Lorentz transformations if the nonrelativistic definitions for momentum and energy would be employed, due to the nonlinear transformations of the particle velocities. This would mean that if momentum and energy conservation would hold for one observer, they would not hold for another observer with different velocity!
However, the conservation laws are preserved if energy and momentum transform linearly, like a 4-vector, under Lorentz transformations. We have already identified 4-velocities $\{U^\mu\} = \gamma(c, \boldsymbol{v})$ with the property $\lim_{\beta\to 0}\boldsymbol{U} = \boldsymbol{v}$.

[14]There is a limit $v \le c$ on the *physical speed* $v = |\boldsymbol{v}|$ of moving objects. No such limit holds for the "eigenspeed" $|\boldsymbol{U}|$, but the speed of signal transmission relative to an observer is v, not $|\boldsymbol{U}|$.

This motivates the definition of the *4-momentum*

$$p^0 = mU^0, \quad \boldsymbol{p} = m\boldsymbol{U},$$

i.e. the relativistic definition of the spatial momentum of a particle of mass m and physical velocity $\boldsymbol{v}$ is

$$\boldsymbol{p} = m\boldsymbol{U} = \gamma m\boldsymbol{v} = \frac{m\boldsymbol{v}}{\sqrt{1-(v^2/c^2)}}. \tag{B.15}$$

The physical meaning of the fourth component

$$p^0 = mU^0 = \gamma mc = \frac{mc}{\sqrt{1-(v^2/c^2)}}$$

can be inferred from the nonrelativistic limit: $v \ll c$ yields

$$p^0 \simeq mc\left(1+\frac{v^2}{2c^2}\right).$$

This motivates the identification of cp^0 with the energy of a particle of mass m and speed v:

$$E = cp^0 = \gamma mc^2 = \frac{mc^2}{\sqrt{1-(v^2/c^2)}}. \tag{B.16}$$

Division of the two equations (B.15) and (B.16) yields

$$\boldsymbol{v} = c^2\frac{\boldsymbol{p}}{E}, \tag{B.17}$$

and subtracting squares yields the relativistic dispersion relation

$$E^2 - c^2\boldsymbol{p}^2 = m^2c^4. \tag{B.18}$$

This is usually written as $p_\mu p^\mu = -m^2c^2$.
Equations (B.18) and (B.17) imply in particular for massless particles the relations $E = cp$ and $v = c$.
For the formulation of the relativistic version of Newton's law, we observe that the rate of change of 4-momentum with eigentime defines a 4-vector with the units of force,

$$f^\mu = \frac{d}{d\tau}m\frac{dx^\mu}{d\tau} = \frac{dp^\mu}{d\tau} = \gamma\frac{d}{dt}p^\mu.$$

It transforms linearly under Lorentz transformations because we divided a 4-vector dx^μ or dp^μ by invariants $d\tau^2$ or $d\tau$, respectively.
By convention one still defines three-dimensional forces according to

$$\boldsymbol{F} = \frac{d}{dt}\boldsymbol{p} = \frac{1}{\gamma}\boldsymbol{f},$$

i.e. $\boldsymbol{F}$ is *not* the spatial component of a 4-vector, but $\boldsymbol{f} = \gamma \boldsymbol{F}$ is.
For the 0-component f^0 we find with the relativistic dispersion relation $E = c\sqrt{\boldsymbol{p}^2 + m^2c^2}$,

$$f^0 = \frac{d}{d\tau} m \frac{dx^0}{d\tau} = \frac{d}{d\tau}\left(m\gamma \frac{dx^0}{dt}\right) = \frac{d}{d\tau}(\gamma mc) = \frac{d}{d\tau}\frac{E}{c} = \frac{d}{d\tau}\sqrt{\boldsymbol{p}^2 + m^2c^2}$$
$$= \frac{\boldsymbol{p}}{\sqrt{\boldsymbol{p}^2 + m^2c^2}} \cdot \frac{d}{d\tau}\boldsymbol{p} = \frac{\boldsymbol{v}}{c} \cdot \frac{d}{d\tau}\boldsymbol{p} = \frac{\boldsymbol{v}}{c} \cdot \boldsymbol{f}. \tag{B.19}$$

The 4-vector of the force is therefore

$$(f^0, \boldsymbol{f}) = (\boldsymbol{\beta} \cdot \boldsymbol{f}, \boldsymbol{f}) = (\gamma \boldsymbol{\beta} \cdot \boldsymbol{F}, \gamma \boldsymbol{F}).$$

Multiplication of (cf. (B.19))

$$\frac{d}{d\tau}\frac{E}{c} = \frac{\boldsymbol{v}}{c} \cdot \boldsymbol{f}$$

with c/γ gives energy balance in conventional form,

$$\frac{d}{dt}E = \frac{c}{\sqrt{\boldsymbol{p}^2 + m^2c^2}} \boldsymbol{p} \cdot \frac{d}{dt}\boldsymbol{p} = \boldsymbol{v} \cdot \frac{d}{dt}\boldsymbol{p} = \boldsymbol{v} \cdot \boldsymbol{F}.$$

Note that the force 4-vector satisfies the relation

$$f_\mu f^\mu = \boldsymbol{f}^2 - (f^0)^2 = \boldsymbol{F}^2, \tag{B.20}$$

i.e. the conventional three-dimensional force $\boldsymbol{F}$ has the interesting property that $|\boldsymbol{F}|$ is Lorentz invariant.
The nonrelativistic Newton equation for motion of a charged particle in electromagnetic fields contains the Lorentz force

$$\boldsymbol{F} = q\boldsymbol{E} + q\boldsymbol{v} \times \boldsymbol{B}.$$

We can get a hint at how the relativistic equation has to look like by expressing this combination of fields in terms of the field strength tensor

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu = \begin{pmatrix} 0 & -E_1/c & -E_2/c & -E_3/c \\ E_1/c & 0 & B_3 & -B_2 \\ E_2/c & -B_3 & 0 & B_1 \\ E_3/c & B_2 & -B_1 & 0 \end{pmatrix}$$

or

$$E^i = cF^i{}_0 = F^i{}_0 \frac{dx^0}{dt}, \quad \varepsilon^i{}_{jk} B^k = F^i{}_j.$$

The latter equation implies

$$(\boldsymbol{v} \times \boldsymbol{B})^i = \varepsilon^i{}_{jk} v^j B^k = F^i{}_j v^j,$$

and therefore

$$F^i = qE^i + q\varepsilon^i{}_{jk}v^j B^k = qF^i{}_0\frac{dx^0}{dt} + qF^i{}_j\frac{dx^j}{dt} = qF^i{}_\nu\frac{dx^\nu}{dt}.$$

This would be a spatial part of a 4-vector if we would not derive with respect to the laboratory time t, but with respect to the eigentime τ of the charged particle:

$$f^i = \gamma F^i = qF^i{}_\nu\frac{dx^\nu}{d\tau}.$$

The time component is then

$$f^0 = qF^0{}_i\frac{dx^i}{d\tau} = q\gamma\frac{1}{c}E_i\frac{dx^i}{dt} = \gamma q\boldsymbol{\beta}\cdot\boldsymbol{E}$$

and the electromagnetic force 4-vector is

$$f^\mu = qF^\mu{}_\nu\frac{dx^\nu}{d\tau} = (\gamma q\boldsymbol{\beta}\cdot\boldsymbol{E}, \gamma q(\boldsymbol{E} + \boldsymbol{v}\times\boldsymbol{B})).$$

The equation of motion of the charged particle in 4-vector notation is therefore

$$m\frac{d^2x^\mu}{d\tau^2} = qF^\mu{}_\nu\frac{dx^\nu}{d\tau},$$

or

$$m\ddot{x}^\mu(\tau) = qF^\mu{}_\nu(x(\tau))\dot{x}^\nu(\tau). \tag{B.21}$$

The time component yields after rescaling with c/γ again the energy balance equation

$$\frac{dE}{dt} = q\boldsymbol{v}\cdot\boldsymbol{E}. \tag{B.22}$$

The spatial part is after rescaling with γ^{-1}:

$$\frac{d}{dt}\boldsymbol{p} = q(\boldsymbol{E} + \boldsymbol{v}\times\boldsymbol{B}), \tag{B.23}$$

The only changes in (B.22,B.23) with respect to the nonrelativistic equations are the velocity dependences of E and $\boldsymbol{p}$:

$$\boldsymbol{p} = \frac{m\boldsymbol{v}}{\sqrt{1-(v^2/c^2)}}, \quad E = \frac{mc^2}{\sqrt{1-(v^2/c^2)}}.$$

The equations (B.21) are completely equivalent to equations (B.23) and (B.22). Note that equation (B.22) is a consequence of (B.23) just like the equation (B.21) with $\mu = 0$ is also a consequence of the other three equations with spatial values for μ.

The virtue of equations (B.21) is the *manifest covariance* of these equations, since linearly transforming equations between 4-vectors must hold in every inertial frame. Contrary to this, covariance is *not apparent* in the equations (B.22,B.23), but since they are equivalent to the manifestly covariant equations (B.21), they also must hold in every inertial frame. Covariance is only *hidden* in the nonlinear transformation behavior of equations (B.22,B.23). However, for practical purposes the equations (B.22,B.23) are often more useful.
The relativistic Lagrange function for a charged particle in terms of the laboratory time t is

$$L_{(t)} = -mc\sqrt{c^2 - \dot{\boldsymbol{x}}^2(t)} + q\dot{\boldsymbol{x}}(t)\cdot\boldsymbol{A}(\boldsymbol{x}(t),t) - q\Phi(\boldsymbol{x}(t),t). \tag{B.24}$$

This yields the canonical momentum

$$\boldsymbol{p}_{can} = \frac{\partial L_{(t)}}{\partial\dot{\boldsymbol{x}}} = \frac{mc\boldsymbol{v}}{\sqrt{c^2-\boldsymbol{v}^2}} + q\boldsymbol{A} = \boldsymbol{p} + q\boldsymbol{A},$$

and the equations of motion in the form (B.23). The relativistic action is

$$\begin{aligned} S &= \int dt\, L_{(t)} = \int\left(-mc\sqrt{c^2dt^2 - d\boldsymbol{x}^2} + qd\boldsymbol{x}\cdot\boldsymbol{A} - qdt\Phi\right) \\ &= \int d\tau\left(-mc\sqrt{-\eta_{\mu\nu}\frac{dx^\mu}{d\tau}\frac{dx^\nu}{d\tau}} + qA_\mu\frac{dx^\mu}{d\tau}\right) = \int d\tau\, L_{(\tau)}. \end{aligned} \tag{B.25}$$

The formulation in terms of the eigentime τ of the particle yields the canonical momentum (use $\eta_{\mu\nu}(dx^\mu/d\tau)(dx^\nu/d\tau) = -c^2$ from the equation $c^2d\tau^2 = -\eta_{\mu\nu}dx^\mu dx^\nu$ after the derivative)

$$p_{can,\mu} = \frac{\partial L_{(\tau)}}{\partial\dot{x}^\mu} = m\eta_{\mu\nu}\frac{dx^\nu}{d\tau} + qA_\mu = p_\mu + qA_\mu,$$

and the Lagrange equation is the manifestly covariant formulation (B.21) of the equations of motion.
The gauge-dependent contributions qA_μ to the conserved momenta disappear in the fully covariant energy-momentum tensor of a classical charged particle of mass m and charge q coupled to electromagnetic fields,

$$\begin{aligned} T_\nu{}^\mu &= \frac{1}{\mu_0}\left(F_{\nu\rho}F^{\mu\rho} - \frac{1}{4}\eta_\nu{}^\mu F_{\rho\sigma}F^{\rho\sigma}\right) + \int d\tau\, mcU_\nu(\tau)U^\mu(\tau)\delta(x - x(\tau)) \\ &= \frac{1}{\mu_0}\left(F_{\nu\rho}F^{\mu\rho} - \frac{1}{4}\eta_\nu{}^\mu F_{\rho\sigma}F^{\rho\sigma}\right) + mc\frac{v_\nu v^\mu}{\sqrt{c^2-v^2}}\delta(\boldsymbol{x} - \boldsymbol{x}(t)). \end{aligned} \tag{B.26}$$

Contrary to the 4-velocity U^μ, the four quantities $v^\mu = dx^\mu/dt = U^\mu/\gamma = (c,\boldsymbol{v})$ are not components of a 4-vector, but still convenient for the representation of the classical energy-momentum tensor after integration over the eigentime of the particle.

The corresponding results for the energy density, energy current density and momentum density of the classical particle plus fields system are

$$\mathcal{H} = c\mathcal{P}^0 = T^{00} = \frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2 + \frac{mc^3}{\sqrt{c^2 - v^2}}\delta(\boldsymbol{x} - \boldsymbol{x}(t)), \tag{B.27}$$

$$\boldsymbol{\mathcal{S}} = c\boldsymbol{e}_i T^{0i} = \frac{1}{\mu_0}\boldsymbol{E} \times \boldsymbol{B} + \frac{mc^3\boldsymbol{v}}{\sqrt{c^2 - v^2}}\delta(\boldsymbol{x} - \boldsymbol{x}(t)), \tag{B.28}$$

$$\boldsymbol{\mathcal{P}} = \frac{1}{c}\boldsymbol{e}_i T^{i0} = \epsilon_0 \boldsymbol{E} \times \boldsymbol{B} + \frac{mc\boldsymbol{v}}{\sqrt{c^2 - v^2}}\delta(\boldsymbol{x} - \boldsymbol{x}(t)) = \frac{1}{c^2}\boldsymbol{\mathcal{S}}, \tag{B.29}$$

and the stress tensor is

$$\underline{T} = \left(\frac{\epsilon_0}{2}\boldsymbol{E}^2 + \frac{1}{2\mu_0}\boldsymbol{B}^2\right)\underline{1} - \epsilon_0 \boldsymbol{E} \otimes \boldsymbol{E} - \frac{1}{\mu_0}\boldsymbol{B} \otimes \boldsymbol{B} + mc\frac{\boldsymbol{v} \otimes \boldsymbol{v}}{\sqrt{c^2 - v^2}}\delta(\boldsymbol{x} - \boldsymbol{x}(t)). \tag{B.30}$$

Appendix C: Completeness of Sturm-Liouville Eigenfunctions

Completeness of eigenfunctions of self-adjoint operators is very important in quantum mechanics. Formulating exact theorems and proofs in general situations is a demanding mathematical problem. However, the setting of Sturm-Liouville problems with homogeneous boundary conditions in one dimension is sufficiently simple to be treated in a single appendix.

Sturm-Liouville problems

Sturm-Liouville problems are linear boundary value problems consisting of a second order differential equation

$$\frac{d}{dx}\left(g(x)\frac{d\psi(x)}{dx}\right) - V(x)\psi(x) + E\varrho(x)\psi(x) = 0 \tag{C.1}$$

in an interval $a \leq x \leq b$ and homogeneous boundary conditions[15] (Sturm 1836, Liouville 1837)

$$\psi(a) = 0, \quad \psi(b) = 0. \tag{C.2}$$

The functions $g(x)$, $V(x)$ and $\varrho(x)$ are real and continuous in $a \leq x \leq b$, and we also assume that the functions $g(x)$ and $\varrho(x)$ are positive in $a \leq x \leq b$.
In ket notation without reference to a particular representation, we would write equation (C.1) as

$$E\varrho(\mathrm{x})|\psi(E)\rangle = \frac{1}{\hbar^2}\mathrm{p}g(\mathrm{x})\mathrm{p}|\psi(E)\rangle + V(\mathrm{x})|\psi(E)\rangle.$$

We can assume $\psi(x) \equiv \langle x|\psi(E)\rangle$ to be a real function, and in this appendix we always assume that a and b are finite. We also require first order differentiability of $g(x)$ and continuity of $V(x)$ and $\varrho(x)$.
We can also assume $\psi'(a) > 0$. We know that $\psi'(a) \neq 0$ because $\psi'(a) = 0$ together with $\psi(a) = 0$ and the Sturm-Liouville equation (C.1) would imply

[15] General Sturm-Liouville boundary conditions would only require linear combinations of $\psi(x)$ and $\psi'(x)$ to vanish at the boundaries, but for our purposes it is sufficient to impose the special conditions $\psi(a) = 0$, $\psi(b) = 0$.

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$\psi(x) = 0$. Furthermore, linearity of the Sturm-Liouville equation implies that we can always change the sign of $\psi(x)$ to ensure $\psi'(a) > 0$.
Multiplication of equation (C.1) with $\psi(x)$ and integration yields

$$H[\psi] \equiv \int_a^b dx \left(g(x)\psi'^2(x) + V(x)\psi^2(x)\right) = E \int_a^b dx\, \varrho(x)\psi^2(x) \equiv E\langle\psi|\psi\rangle$$

where the last equation defines the scalar product

$$\langle\phi|\psi\rangle = \int_a^b dx\, \varrho(x)\phi(x)\psi(x). \tag{C.3}$$

It is easy to prove that (C.3) defines a scalar product since $\langle\psi|\psi\rangle \geq 0$ and $\langle\psi|\psi\rangle = 0 \Leftrightarrow \psi(x) = 0$, and

$$0 \leq \langle\psi + \lambda\phi|\psi + \lambda\phi\rangle = \langle\psi|\psi\rangle + 2\lambda\langle\psi|\phi\rangle + \lambda^2\langle\phi|\phi\rangle \tag{C.4}$$

has a minimum for

$$\lambda = -\frac{\langle\psi|\phi\rangle}{\langle\phi|\phi\rangle},$$

which after substitution in (C.4) yields the Schwarz inequality

$$\langle\psi|\phi\rangle^2 \leq \langle\psi|\psi\rangle\langle\phi|\phi\rangle.$$

The Sturm-Liouville equation (C.1) arises as an Euler-Lagrange equation from variation of the action

$$\begin{aligned} S[\psi] &= E\langle\psi|\psi\rangle - H[\psi] \\ &= \int_a^b dx \left(E\varrho(x)\psi^2(x) - g(x)\psi'^2(x) - V(x)\psi^2(x)\right) \end{aligned} \tag{C.5}$$

with fixed endpoints $\psi(a)$ and $\psi(b)$.
The stationary values of $S[\psi]$ for arbitrary fixed endpoints $\psi(a)$ and $\psi(b)$ are

$$S[\psi]\Big|_{\text{on-shell}} = g(a)\psi(a)\psi'(a) - g(b)\psi(b)\psi'(b),$$

where the designation "on-shell" means that $\psi(x)$ satisfies the Euler-Lagrange equation (C.1) of $S[\psi]$.
If we think of the Sturm-Liouville problem as a one-dimensional scalar field theory, $G(x) = 1/4g^2(x)$ would play the role of a metric in $a \leq x \leq b$ and $H[\psi]$ would be the energy of the field $\psi(x)$ if $\psi(x)$ is normalized, $\langle\psi|\psi\rangle = 1$.
Suppose $\psi_i(x)$ and $\psi_j(x)$ are solutions of the Sturm-Liouville problem (C.1,C.2) with eigenvalues E_i and E_j, respectively. Use of the Sturm-Liouville equation (C.1) and partial integration yields

$$E_i \int_a^x d\xi\, \varrho(\xi)\psi_j(\xi)\psi_i(\xi) = \int_a^x d\xi\, \psi_j(\xi) \left[V(\xi)\psi_i(\xi) - \frac{d}{d\xi}\left(g(\xi)\frac{d}{d\xi}\psi_i(\xi)\right)\right]$$

$$= \int_a^x d\xi \left(V(\xi)\psi_j(\xi)\psi_i(\xi) + g(\xi)\psi_j'(\xi)\psi_i'(\xi) \right) - g(x)\psi_j(x)\frac{d}{dx}\psi_i(x),$$

and after another partial integration we find

$$(E_i - E_j) \int_a^x d\xi\, \varrho(\xi)\psi_i(\xi)\psi_j(\xi) = g(x)\left(\psi_i(x)\frac{d}{dx}\psi_j(x) - \psi_j(x)\frac{d}{dx}\psi_i(x) \right). \tag{C.6}$$

This equation implies for $E_i = E_j$

$$\frac{d}{dx}\ln\psi_i(x) = \frac{d}{dx}\ln\psi_j(x),$$

i.e. $\psi_i(x)$ has to be proportional to $\psi_j(x)$: There is no degeneracy of eigenvalues in the one-dimensional Sturm-Liouville problem.
For $x = b$, equation (C.6) implies the orthogonality property

$$(E_i - E_j)\langle\psi_i|\psi_j\rangle = 0$$

and taking into account the absence of degeneracy yields

$$\langle\psi_i|\psi_j\rangle \propto \delta_{ij}.$$

Liouville's normal form of Sturm's equation

We can gauge the functions $g(x)$ and $\varrho(x)$ away through a transformation of variables

$$x \to X = \int_a^x d\xi \sqrt{\frac{\varrho(\xi)}{g(\xi)}}, \quad \psi(x) \to \Psi(X) = (\varrho(x)g(x))^{1/4}\,\psi(x).$$

This yields

$$0 \le X \le B = \int_a^b dx \sqrt{\frac{\varrho(x)}{g(x)}}, \quad \Psi(0) = 0, \quad \Psi(B) = 0,$$

and the Sturm-Liouville equation (C.1) assumes the form of a one-dimensional Schrödinger equation,

$$\frac{d^2}{dX^2}\Psi(X) - V(X)\Psi(X) + E\Psi(X) = 0 \tag{C.7}$$

with

$$V(X) = \frac{V(x)}{\varrho(x)} + \frac{g(x)\varrho''(x) + \varrho(x)g''(x)}{4\varrho^2(x)} - \frac{5g(x)\varrho'^2(x)}{16\varrho^3(x)} - \frac{g'^2(x)}{16g(x)\varrho(x)} + \frac{g'(x)\varrho'(x)}{8\varrho^2(x)}.$$

Second order differentiability of $\varrho(x)$ and $g(x)$ is usually assumed. However, we only have to require continuity of the positive functions $\varrho(x)$ and $g(x)$ since we can deal with δ-function singularities in one-dimensional potentials,.
Equation (C.7) is *Liouville's normal form* of the Sturm-Liouville equation.

Nodes of Sturm-Liouville eigenfunctions

For the following reasoning we assume that we have smoothly continued the functions $V(x)$, $\varrho(x) > 0$ and $g(x) > 0$ for all values of $x \in \mathbb{R}$. It does not matter how we do that.

To learn more about the nodes of the eigenfunctions $\psi_i(x)$ of the Sturm-Liouville boundary value problem, let us now assume that $\psi(x, \lambda)$ and $\psi(x, \mu)$ are solutions of the incomplete initial value problems

$$\lambda\varrho(x)\psi(x,\lambda) = V(x)\psi(x,\lambda) - \frac{d}{dx}\left(g(x)\frac{d\psi(x,\lambda)}{dx}\right), \quad \psi(a,\lambda) = 0, \quad \text{(C.8)}$$

$$\mu\varrho(x)\psi(x,\mu) = V(x)\psi(x,\mu) - \frac{d}{dx}\left(g(x)\frac{d\psi(x,\mu)}{dx}\right), \quad \psi(a,\mu) = 0, \quad \text{(C.9)}$$

with $\lambda > \mu$, *but contrary to the boundary value problem (C.1,C.2) we do not impose any conditions at* $x = b$. In that case there exist solutions to the Sturm-Liouville equations for arbitrary values of the parameters λ, μ, and we can again require

$$\left.\frac{d\psi(x,\lambda)}{dx}\right|_{x=a} > 0, \quad \left.\frac{d\psi(x,\mu)}{dx}\right|_{x=a} > 0.$$

We recall the following facts from the theory of differential equations: The solution $\psi(x, \lambda)$ to the initial value problem (C.8) is unique up to a multiplicative constant, and $\psi(x, \lambda)$ depends continuously on the parameter λ.

The last fact is important, because it implies that the nodes $y(\lambda)$ of $\psi(x, \lambda)$, $\psi(y(\lambda), \lambda) = 0$, depend continuously on λ. Continuity of $y(\lambda)$ is used in the demonstration below that the boundary value problem (C.1,C.2) has a solution for every value of b.

Multiplication of equation (C.8) with $\psi(x, \mu)$ and equation (C.9) with $\psi(x, \lambda)$, integration from a to $x > a$, and subtraction of the equations yields

$$\begin{aligned}
&(\lambda - \mu)\int_a^x d\xi\, \varrho(\xi)\psi(\xi,\lambda)\psi(\xi,\mu) \\
&= \int_a^x d\xi \left[\psi(\xi,\lambda)\frac{d}{d\xi}\left(g(\xi)\frac{d\psi(\xi,\mu)}{d\xi}\right) - \psi(\xi,\mu)\frac{d}{d\xi}\left(g(\xi)\frac{d\psi(\xi,\lambda)}{d\xi}\right)\right] \\
&= g(x)\left(\psi(x,\lambda)\frac{d\psi(x,\mu)}{dx} - \psi(x,\mu)\frac{d\psi(x,\lambda)}{dx}\right). \qquad \text{(C.10)}
\end{aligned}$$

Now assume that $y(\mu)$ is the first node of $\psi(x, \mu)$ larger than a:

$$\psi(y(\mu),\mu) = 0, \quad y(\mu) > a.$$

Substituting $x = y(\mu)$ in (C.10) yields

$$(\lambda - \mu)\int_a^{y(\mu)} dx\, \varrho(x)\psi(x,\lambda)\psi(x,\mu) = g(y(\mu))\psi(y(\mu),\lambda)\left.\frac{d\psi(x,\mu)}{dx}\right|_{x=y(\mu)}. \qquad \text{(C.11)}$$

We know that

$$(\lambda - \mu)\varrho(x)\psi(x,\mu) > 0$$

for $a < x < y(\mu)$ and that

$$g(y(\mu))\frac{d\psi(x,\mu)}{dx}\bigg|_{x=y(\mu)} < 0.$$

This implies $\psi(x,\lambda)$ must change its sign at least once for $a < x < y(\mu)$, and in particular $y(\lambda) < y(\mu)$:
The location of the leftmost node $y(\lambda) > a$ of the function $\psi(x,\lambda)$ moves closer to a if λ increases.
We are not really concerned with differentiability properties of the leftmost node $y(\lambda)$, but we can express the previous observation also as

$$y(\lambda) > a, \quad \frac{dy(\lambda)}{d\lambda} < 0.$$

Now assume that λ is small enough[16] so that even $y(\lambda) > b$. Then we can increase the parameter λ until we reach a value $\lambda = E_1$ such that $y(E_1) = b$. This is then the lowest eigenvalue of our original Sturm-Liouville boundary value problem (C.1), and the corresponding eigenfunction is

$$\psi_1(x) = \psi(x, \lambda = E_1). \tag{C.12}$$

The eigenfunction $\psi_1(x)$ for the lowest eigenvalue E_1 has no nodes in $a < x < b$.
Now we consider the first and the second node of $\psi(x,\mu)$ for $x > a$,

$$a < y(\mu) \equiv y_1(\mu) < y_2(\mu), \quad \psi(y_1(\mu),\mu) = 0, \quad \psi(y_2(\mu),\mu) = 0,$$

and we integrate from $y_1(\mu)$ to $y_2(\mu)$,

$$\begin{aligned}
&(\lambda - \mu)\int_{y_1(\mu)}^{y_2(\mu)} dx\, \varrho(x)\psi(x,\lambda)\psi(x,\mu) \\
&= \int_{y_1(\mu)}^{y_2(\mu)} dx \left[\psi(x,\lambda)\frac{d}{dx}\left(g(x)\frac{d\psi(x,\mu)}{dx}\right) - \psi(x,\mu)\frac{d}{dx}\left(g(x)\frac{d\psi(x,\lambda)}{dx}\right)\right] \\
&= g(y_2(\mu))\ \psi(y_2(\mu),\lambda)\frac{d\psi(x,\mu)}{dx}\bigg|_{x=y_2(\mu)} \\
&\quad - g(y_1(\mu))\ \psi(y_1(\mu),\lambda)\frac{d\psi(x,\mu)}{dx}\bigg|_{x=y_1(\mu)}.
\end{aligned}$$

[16] The alert reader might worry that all $y(\lambda)$ might be smaller than b, so that there is no finite small value λ with $y(\lambda) > b$, or otherwise that all $y(\lambda)$ might be larger than b, so that no finite value E_1 with $y(E_1) = b$ would exist. These cases can be excluded through Sturm's comparison theorem, to be discussed later.

We know

$$(\lambda - \mu)\varrho(x)\psi(x,\mu) < 0$$

for $y_1(\mu) < x < y_2(\mu)$, and

$$g(y_1(\mu))\frac{d\psi(x,\mu)}{dx}\bigg|_{x=y_1(\mu)} < 0, \quad g(y_2(\mu))\frac{d\psi(x,\mu)}{dx}\bigg|_{x=y_2(\mu)} > 0.$$

This tells us that $\psi(x,\lambda)$ has to change sign in the interval $y_1(\mu) < x < y_2(\mu)$, i.e. it must have at least one node there. We know that the first node $y_1(\lambda) < y_1(\mu)$ is outside of this interval. Therefore we can infer that at least the second node $y_2(\lambda)$ of $\psi(x,\lambda)$ must be smaller than $y_2(\mu)$: $y_2(\lambda) < y_2(\mu)$. We can repeat this reasoning for the pair of adjacent nodes $y_{n-1}(\mu)$, $y_n(\mu)$ of $\psi(x,\mu)$, and we always find for $\lambda > \mu$ that $y_n(\lambda) < y_n(\mu)$,

$$a < y_n(\lambda), \quad \psi(y_n(\lambda),\lambda) = 0, \quad \frac{dy_n(\lambda)}{d\lambda} < 0.$$

All nodes of the function $\psi(x,\lambda)$ on the right hand side of $x = a$ move closer to a if λ increases.

Therefore we can repeat the reasoning above which had let us to the first solution $\psi_1(x)$ with eigenvalue E_1 of our Sturm-Liouville problem. To find the second eigenfunction, we increase $\lambda > E_1$ until we hit a value $\lambda = E_2$ such that $y_2(E_2) = b$, and the corresponding eigenfunction

$$\psi_2(x) = \psi(x, E_2)$$

will have exactly one node $y_1(E_2)$ in the interval, $a < y_1(E_2) < b$.

The corresponding result for $y_n(\lambda)$ tells us that in the nth step we will find a parameter $\lambda = E_n$ with $y_n(E_n) = b$ and eigenfunction

$$\psi_n(x) = \psi(x, E_n),$$

and this function will have $n-1$ nodes $a < y_1(E_n) < y_2(E_n) < \ldots < y_{n-1}(E_n) < y_n(E_n) = b$ inside the interval.

Sturm's comparison theorem and estimates for the locations of the nodes $y_n(\lambda)$

Sturm's comparison theorem makes a statement about the change of the nodes $y_n > a$ of the solution $\psi(x,\lambda)$ of

$$\frac{d}{dx}\left(g(x)\frac{d\psi(x,\lambda)}{dx}\right) + (\lambda\varrho(x) - V(x))\,\psi(x,\lambda) = 0, \quad \psi(a,\lambda) = 0, \quad \text{(C.13)}$$

if the functions $g(x)$, $\varrho(x)$ and $V(x)$ change. To prove the comparison theorem, we do *not* use Liouville's normal form, but perform the following simple transformation of variables,

$$X = \int_a^x \frac{dx'}{g(x')}, \quad \Psi(X,\lambda) = \psi(x,\lambda).$$

This transforms (C.13) into the following form,

$$\frac{d^2\Psi(X,\lambda)}{dX^2} + (\lambda R(X) - V(X))\,\Psi(X,\lambda) = 0, \quad \Psi(0,\lambda) = 0, \tag{C.14}$$

$$R(X) = g(x)\varrho(x) > 0, \quad V(X) = g(x)V(x),$$

and the nodes $Y_n > 0$ of $\Psi(X,\lambda)$ are related to the nodes $y_n > a$ of $\psi(x,\lambda)$ through

$$Y_n = \int_a^{y_n} \frac{dx}{g(x)}. \tag{C.15}$$

Now we consider another Sturm-Liouville problem of the form (C.14), but with different functions

$$\lambda S(X) - W(X) > \lambda R(X) - V(X),$$

$$\frac{d^2\Phi(X,\lambda)}{dX^2} + (\lambda S(X) - W(X))\,\Phi(X,\lambda) = 0, \quad \Phi(0,\lambda) = 0, \tag{C.16}$$

and we denote the positive nodes of $\Phi(X,\lambda)$ with Z_n. We also require again $\Psi'(0) > 0$, $\Phi'(0) > 0$. Equations (C.14,C.16) imply

$$\int_{Y_{n-1}}^{Y_n} dX\,[V(X) - W(X) - \lambda\,(R(X) - S(X))]\,\Psi(X,\lambda)\Phi(X,\lambda)$$

$$= \Phi(Y_n,\lambda)\,\frac{d\Psi(X,\lambda)}{dX}\bigg|_{X=Y_n} - \Phi(Y_{n-1},\lambda)\,\frac{d\Psi(X,\lambda)}{dX}\bigg|_{X=Y_{n-1}}. \tag{C.17}$$

The following terms in (C.17) have all the same sign,

$$[V(X) - W(X) - \lambda\,(R(X) - S(X))]\,\Psi(X,\lambda)\Big|_{Y_{n-1}<X<Y_n},$$

$$\frac{d\Psi(X,\lambda)}{dX}\bigg|_{X=Y_{n-1}}, \quad -\frac{d\Psi(X,\lambda)}{dX}\bigg|_{X=Y_n}.$$

This implies that $\Phi(X,\lambda)$ must change its sign in $Y_{n-1} < X < Y_n$, and since this must hold for every $n \geq 1$ we find

$$Z_n < Y_n.$$

Increasing $\lambda R(X) - V(X)$ moves the nodes $Y_n > 0$ of the function $\Psi(X,\lambda)$ to the left. From this we can first derive bounds for the nodes $Y_n > 0$ which arise from the nodes of the solutions of

$$\begin{aligned}&\Psi''_{min}(X,\lambda) + (\lambda R_{max} - V_{min})\,\Psi_{min}(X,\lambda)\\ &= \Psi''_{min}(X,\lambda) + g_{max}\,(\lambda\varrho_{max} - U_{min})\,\Psi_{min}(X,\lambda) = 0,\\ &\Psi_{min}(0,\lambda) = 0,\end{aligned} \tag{C.18}$$

and

$$\begin{aligned}&\Psi''_{max}(X,\lambda) + (\lambda R_{min} - V_{max})\,\Psi_{max}(X,\lambda)\\ &= \Psi''_{max}(X,\lambda) + g_{min}\,(\lambda\varrho_{min} - U_{max})\,\Psi_{max}(X,\lambda) = 0,\\ &\Psi_{max}(0,\lambda) = 0.\end{aligned} \tag{C.19}$$

Here we use the bounds of the continuous functions $g(x)$, $V(x)$, $\varrho(x)$ on $a \le x \le b$,

$$0 < g_{min} \le g(x) \le g_{max}, \quad U_{min} \le V(x) \le U_{max}, \quad 0 < \varrho_{min} \le \varrho(x) \le \varrho_{max}.$$

The solutions of both equations (C.18) and (C.19) have nodes if (recall that both $g(x) > 0$ and $\varrho(x) > 0$)

$$\lambda > U_{min}/\varrho_{max},$$

and the two solutions are

$$\Psi_{min}(X,\lambda) \propto \sin\left(\sqrt{g_{max}\,(\lambda\varrho_{max} - U_{min})}X\right),$$

$$\Psi_{max}(X,\lambda) \propto \sin\left(\sqrt{g_{min}\,(\lambda\varrho_{min} - U_{max})}X\right).$$

This yields bounds for the nodes $Y_n > 0$ of $\Psi(X,\lambda)$,

$$\frac{n\pi}{\sqrt{g_{max}\,(\lambda\varrho_{max} - U_{min})}} \le Y_n \le \frac{n\pi}{\sqrt{g_{min}\,(\lambda\varrho_{min} - U_{max})}}. \tag{C.20}$$

However, we also know from equation (C.15) that $g_{min}Y_n \le y_n - a \le g_{max}Y_n$, and therefore[17]

$$a + \frac{g_{min}n\pi}{\sqrt{g_{max}\,(\lambda\varrho_{max} - U_{min})}} \le y_n \le a + \frac{g_{max}n\pi}{\sqrt{g_{min}\,(\lambda\varrho_{min} - U_{max})}}. \tag{C.21}$$

This implies in particular that *there is no accumulation point for the nodes y_n of $\psi(x,\lambda)$, and y_n must grow like n for large n.*

For our previous proof that $\psi_1(x)$ (C.12) has its first node at $y_1 = b$, we needed the assumption that there are small enough values of λ such that the first node $y_1(\lambda)$ of $\psi(x,\lambda)$ satisfies $y_1(\lambda) > b$. We can now confirm that from the lower bound in (C.21). It will suffice to choose

$$\frac{U_{min}}{\varrho_{max}} < \lambda < \frac{U_{min}}{\varrho_{max}} + \frac{g_{min}^2\pi^2}{\varrho_{max}g_{max}(b-a)^2}. \tag{C.22}$$

We also needed the assumption that for large enough λ the first node $y_1(\lambda) > a$ would be smaller than b. This is easily confirmed from the upper bound in (C.21). It is sufficient to choose

$$\lambda > \frac{U_{max}}{\varrho_{min}} + \frac{g_{max}^2\pi^2}{\varrho_{min}g_{min}(b-a)^2}. \tag{C.23}$$

[17] These bounds can be strengthened by a longer proof, but the present result is completely sufficient for our purposes.

Estimates for the eigenvalues of the Sturm-Liouville problem

We have found that the Sturm-Liouville boundary value problem (C.1,C.2) has an increasing, non-degenerate set of eigenvalues

$$E_1 < E_2 < \dots$$

and arises as an Euler-Lagrange equation for the action

$$\begin{aligned} S[\psi] &= E\langle\psi|\psi\rangle - H[\psi] \\ &= \int_a^b dx \left(E\varrho(x)\psi^2(x) - g(x)\psi'^2(x) - V(x)\psi^2(x)\right). \end{aligned} \tag{C.24}$$

For every continuous function $\psi(x)$ in $a \le x \le b$ we define the normalized function

$$\hat{\psi}(x) = \frac{\psi(x)}{\sqrt{\langle\psi|\psi\rangle}}.$$

Since $S[\psi]$ is homogeneous in ψ, $\psi(x)$ is a stationary point of $S[\psi]$ if and only if $\hat{\psi}(x)$ is a stationary point of

$$S[\hat{\psi}] = E - H[\hat{\psi}],$$

which implies also that $\hat{\psi}(x)$ is a stationary point of the functional

$$H[\hat{\psi}] = \frac{H[\psi]}{\langle\psi|\psi\rangle} = \frac{\int_a^b dx\,[g(x)\psi'^2(x) + V(x)\psi^2(x)]}{\int_a^b dx\,\varrho(x)\psi^2(x)}. \tag{C.25}$$

We have already found that there is a discrete subset $\hat{\psi}_n(x)$, $n \in \mathbb{N}$, of stationary points of $H[\hat{\psi}]$ which satisfy the boundary conditions $\hat{\psi}_n(a) = 0$, $\hat{\psi}_n(b) = 0$, and are mutually orthogonal,

$$\langle\hat{\psi}_m|\hat{\psi}_n\rangle = \delta_{mn}.$$

Use of the Sturm-Liouville equation and the boundary conditions yields the values of the functional $H[\hat{\psi}]$ at the stationary points $\hat{\psi}_n(x)$,

$$H[\hat{\psi}_n] = E_n.$$

We already know $E_1 < E_2 < \dots$, and therefore we have found that the functional $H[\hat{\psi}]$ has a minimum

$$H[\hat{\psi}_1] = E_1$$

on the space of functions

$$\mathcal{F}_{a,b} = \{\psi(x), a \le x \le b | \psi(a) = 0, \psi(b) = 0, \langle\psi|\psi\rangle = 1\},$$

and in general we have a minimum

$$H[\hat{\psi}_n] = E_n$$

on the space of functions

$$\mathcal{F}_{a,b}^{(n)} = \{\psi(x), a \le x \le b | \psi(a) = 0, \psi(b) = 0, \langle\psi|\psi\rangle = 1, \langle\psi_i|\psi\rangle = 0, \\ 1 \le i \le n-1\}.$$

The explicit form of $H[\hat{\psi}]$ in equation (C.25) shows that all the eigenvalues E_n increase if $g(x)$ increases or $V(x)$ increases or $\varrho(x)$ decreases.
However, those continuous functions must be bounded on the finite interval $a \le x \le b$,

$$0 < g_{min} \le g(x) \le g_{max}, \quad U_{min} \le V(x) \le U_{max},$$

$$0 < \varrho_{min} \le \varrho(x) \le \varrho_{max}.$$

Therefore we can replace those functions with their extremal values to derive estimates for the eigenvalues E_n.
The Sturm-Liouville problems for the extremal values are

$$g_{min/max}\psi_n''(x) + \left(E_{n,min/max}\varrho_{max/min} - U_{min/max}\right)\psi_n(x) = 0,$$

$$\psi_n(a) = 0, \quad \psi_n(b) = 0,$$

with solutions

$$\psi_n(x) \propto \sin\left(n\pi\frac{x-a}{b-a}\right)$$

and corresponding eigenvalues

$$E_{n,min/max} = \frac{1}{\varrho_{max/min}}\left(U_{min/max} + g_{min/max}\frac{n^2\pi^2}{(b-a)^2}\right).$$

This implies the bounds

$$\frac{1}{\varrho_{max}}\left(U_{min} + g_{min}\frac{n^2\pi^2}{(b-a)^2}\right) \le E_n \le \frac{1}{\varrho_{min}}\left(U_{max} + g_{max}\frac{n^2\pi^2}{(b-a)^2}\right). \tag{C.26}$$

In particular, *at most a finite number of the lowest eigenvalues E_n can be negative, and the eigenvalues for large n must grow like n^2.*
Both of these observations are crucial for the proof that the set $\psi_n(x)$ of eigenfunctions of the Sturm-Liouville problem (C.1,C.2) provide a complete basis for the expansion of piecewise continuous functions in $a \le x \le b$.

Completeness of Sturm-Liouville eigenstates

We now assume that the Sturm-Liouville eigenstates are normalized,

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}.$$

Let $\phi(x)$ be an arbitrary smooth function on $a \le x \le b$ with $\phi(a) = 0$ and $\phi(b) = 0$, and define

$$\varphi_n(x) = \phi(x) - \sum_{i=1}^{n} \psi_i(x)\langle\psi_i|\phi\rangle.$$

Then we have

$$0 \le \langle\varphi_n|\varphi_n\rangle = \langle\phi|\phi\rangle - \sum_{i=1}^{n}\langle\psi_i|\phi\rangle^2,$$

i.e. for all n we have a *Bessel inequality*

$$\langle\phi|\phi\rangle \ge \sum_{i=1}^{n}\langle\psi_i|\phi\rangle^2.$$

We also have $\langle\varphi_n|\psi_i\rangle = 0$, $1 \le i \le n$, and $\varphi_n(a) = 0$, $\varphi_n(b) = 0$, i.e.

$$\varphi_n(x) \in \mathcal{F}_{a,b}^{(n+1)}.$$

Therefore the minimum property of the eigenvalue E_{n+1} implies

$$E_{n+1} \le \frac{H[\varphi_n]}{\langle\varphi_n|\varphi_n\rangle}. \tag{C.27}$$

We have

$$\begin{aligned} H[\varphi_n] = H[\phi] - 2\sum_{i=1}^{n}\langle\psi_i|\phi\rangle \int_a^b dx\,(g(x)\phi'(x)\psi_i'(x) + V(x)\phi(x)\psi_i(x)) \\ + \sum_{i,j=1}^{n}\langle\psi_i|\phi\rangle\langle\psi_j|\phi\rangle \int_a^b dx\,\left(g(x)\psi_i'(x)\psi_j'(x) + V(x)\psi_i\psi_j(x)\right). \end{aligned}$$

In the first sum, partial integration and use of the Sturm-Liouville equation yields

$$\begin{aligned} \int_a^b dx\,(g(x)\phi'(x)\psi_i'(x) + V(x)\phi(x)\psi_i(x)) &= E_i\int_a^b dx\,\varrho(x)\phi(x)\psi_i(x) \\ &= E_i\langle\psi_i|\phi\rangle. \end{aligned}$$

In the double sum, partial integration and use of the Sturm-Liouville equation yields

$$\begin{aligned} \int_a^b dx\,\left(g(x)\psi_i'(x)\psi_j'(x) + V(x)\psi_i\psi_j(x)\right) &= E_i\int_a^b dx\,\varrho(x)\psi_i(x)\psi_j(x) \\ &= E_i\delta_{ij}. \end{aligned}$$

This implies

$$H[\varphi_n] = H[\phi] - \sum_{i=1}^{n} E_i \langle \psi_i | \phi \rangle^2. \tag{C.28}$$

Since at most finitely many of the eigenvalues E_i can be negative, equation (C.28) tells us that the functional $H[\varphi_n]$ must remain bounded from above for $n \to \infty$, e.g. for

$$E_1 < E_2 < \cdots < E_N < 0 \leq E_{N+1} < \ldots$$

we have the bound

$$H[\varphi_n] \leq H[\phi] + \sum_{i=1}^{N} |E_i| \langle \psi_i | \phi \rangle^2.$$

On the other hand, equation (C.27) yields for $n > N$ (to ensure $E_{n+1} > 0$),

$$\langle \varphi_n | \varphi_n \rangle = \langle \phi | \phi \rangle - \sum_{i=1}^{n} \langle \psi_i | \phi \rangle^2 \leq \frac{H[\varphi_n]}{E_{n+1}}$$

and since E_{n+1} grows like n^2 for large n while $H[\varphi_n]$ must remain bounded, we find the completeness relation

$$\lim_{n\to\infty} \langle \varphi_n | \varphi_n \rangle = \lim_{n\to\infty} \int_a^b dx\, \varrho(x) \left(\phi(x) - \sum_{i=1}^{n} \psi_i(x) \langle \psi_i | \phi \rangle \right)^2 = 0 \tag{C.29}$$

or equivalently,

$$\langle \phi | \phi \rangle = \lim_{n\to\infty} \sum_{i=1}^{n} \langle \phi | \psi_i \rangle \langle \psi_i | \phi \rangle.$$

Completeness of the series

$$\sum_{i=1}^{\infty} \psi_i(x) \langle \psi_i | \phi \rangle \sim \phi(x)$$

in the sense of equation (C.29) is denoted as *completeness in the mean*, and is sometimes also expressed as

$$\text{l.i.m.}_{n\to\infty} \sum_{i=1}^{n} \psi_i(x) \langle \psi_i | \phi \rangle = \phi(x),$$

where l.i.m. stands for "limit in the mean". Completeness in the mean says that the series $\sum_{i=1}^{\infty} \psi_i(x) \langle \psi_i | \phi \rangle$ approximates $\phi(x)$ in the least squares sense.

Completeness in the mean also implies for the two piecewise continuous functions f and g

$$f(x) \pm g(x) \sim \sum_{i=1}^{\infty} \psi_i(x)\langle\psi_i|f\rangle \pm \sum_{i=1}^{\infty} \psi_i(x)\langle\psi_i|g\rangle$$

and therefore

$$\langle f|g\rangle = \frac{1}{4}\left(\langle f+g|f+g\rangle - \langle f-g|f-g\rangle\right) = \lim_{n\to\infty} \sum_{i=1}^{n} \langle f|\psi_i\rangle\langle\psi_i|g\rangle. \quad \text{(C.30)}$$

Completeness in the sense of (C.30) is enough for quantum mechanics, because it says that we can use the completeness relation

$$\underline{1} = \lim_{n\to\infty} \sum_{i=1}^{n} |\psi_i\rangle\langle\psi_i|$$

in the calculation of matrix elements between sufficiently smooth functions (where "sufficiently smooth = continuously differentiable to a required order" depends on the operators we use). This is all that is really needed in quantum mechanics. However, for piecewise smooth functions, the relation also holds pointwise almost everywhere (see remark 3 below).
I would like to add a few remarks:
1. The completeness property (C.29) also applies to piecewise continuous functions in $a \le x \le b$ and functions which do not vanish at the boundary points, because every piecewise continuous function can be approximated in the mean by a smooth function which vanishes at the boundaries.
2. If $\phi(x)$ is a smooth function satisfying the Sturm-Liouville boundary conditions, as we have assumed in the derivation of (C.29), the series under the integral sign will even converge uniformly to $\phi(x)$,

$$\lim_{n\to\infty} \sum_{i=1}^{n} \psi_i(x)\langle\psi_i|\phi\rangle = \phi(x),$$

i.e. for all $a \le x \le b$ and all values $\epsilon > 0$, there exists an $n(\epsilon)$ such that

$$\left|\phi(x) - \sum_{i=1}^{n} \psi_i(x)\langle\psi_i|\phi\rangle\right| < \epsilon \quad \text{if} \quad n \ge n(\epsilon). \quad \text{(C.31)}$$

Uniformity of the convergence refers to the fact that the same $n(\epsilon)$ ensures (C.31) for all $a \le x \le b$.
3. If $\phi(x)$ is piecewise smooth in $a \le x \le b$, it can still be expanded pointwise in Sturm-Liouville eigenstates. Except for points of discontinuity of $\phi(x)$, and except for the boundary points if $\phi(x)$ does not satisfy the same boundary conditions as the eigenfunctions $\psi_i(x)$, the expansion

$$\phi(x) = \lim_{n\to\infty} \sum_{i=1}^{n} \psi_i(x)\langle\psi_i|\phi\rangle$$

holds pointwise, and the series converges uniformly to $\phi(x)$ in every closed interval which excludes discontinuities of $\phi(x)$ (and the series converges to the arithmetic mean in the points of discontinuity). The boundary points must also be excluded if $\phi(x)$ does not satisfy the Sturm-Liouville boundary conditions.

Appendix D: Properties of Hermite Polynomials

We use the following equation as a definition of Hermite polynomials,

$$H_n(x) = \exp\left(\frac{1}{2}x^2\right)\left(x - \frac{d}{dx}\right)^n \exp\left(-\frac{1}{2}x^2\right), \tag{D.1}$$

because we initially encountered them in this form in the solution of the harmonic oscillator in Chapter 6. We can use the identity

$$\left(x + \frac{d}{dx}\right) f(x) = \exp\left(-\frac{1}{2}x^2\right)\frac{d}{dx}\left[\exp\left(\frac{1}{2}x^2\right) f(x)\right]$$

to rewrite equation (D.1) in the form

$$\begin{aligned} H_n(x) &= \exp\left(\frac{1}{2}x^2\right)\left[2x - \exp\left(-\frac{1}{2}x^2\right)\frac{d}{dx}\exp\left(\frac{1}{2}x^2\right)\right]^n \exp\left(-\frac{1}{2}x^2\right) \\ &= \left[\exp\left(\frac{1}{2}x^2\right)\left[2x - \exp\left(-\frac{1}{2}x^2\right)\frac{d}{dx}\exp\left(\frac{1}{2}x^2\right)\right]\exp\left(-\frac{1}{2}x^2\right)\right]^n \\ &= \left(2x - \frac{d}{dx}\right)^n 1, \end{aligned} \tag{D.2}$$

or we can use the identity

$$\left(x - \frac{d}{dx}\right) f(x) = -\exp\left(\frac{1}{2}x^2\right)\frac{d}{dx}\left[\exp\left(-\frac{1}{2}x^2\right) f(x)\right]$$

to rewrite equation (D.1) in the Rodrigues form

$$H_n(x) = \exp\left(x^2\right)\left(-\frac{d}{dx}\right)^n \exp\left(-x^2\right). \tag{D.3}$$

The Rodrigues formula implies

$$\begin{aligned} \sum_{n=0}^{\infty} H_n(x)\frac{z^n}{n!} &= \sum_{n=0}^{\infty}\left[\exp\left(x^2\right)\frac{\partial^n}{\partial z^n}\exp\left(-(x-z)^2\right)\right]_{z=0}\frac{z^n}{n!} \\ &= \exp\left(x^2\right)\exp\left(-(x-z)^2\right) = \exp\left(2xz - z^2\right). \end{aligned} \tag{D.4}$$

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Graduate Texts in Physics, DOI 10.1007/978-1-4419-8077-9,
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The residue theorem then also yields the representation

$$H_n(x) = \frac{n!}{2\pi \mathrm{i}} \oint dz \, \frac{\exp(2xz - z^2)}{z^{n+1}}, \tag{D.5}$$

where the integration contour encloses $z = 0$ in the positive sense of direction, i.e. counter clockwise.
Another useful integral representation for the Hermite polynomials follows from (D.2) and the equation

$$\begin{aligned}\int_{-\infty}^{\infty} du \, (2u)^n \exp\bigl(-(u+v)^2\bigr) &= \int_{-\infty}^{\infty} du \left(-2v - \frac{\partial}{\partial v}\right)^n \exp\bigl(-(u+v)^2\bigr) \\ &= \left(-2v - \frac{\partial}{\partial v}\right)^n \sqrt{\pi}.\end{aligned}$$

This yields in particular for $v = -\mathrm{i}x$,

$$\int_{-\infty}^{\infty} du \, (2u)^n \exp\bigl(-(u - \mathrm{i}x)^2\bigr) = \mathrm{i}^n \sqrt{\pi} H_n(x). \tag{D.6}$$

Combination of equations (D.4) and (D.6) yields Mehler's formula[18],

$$\begin{aligned}\sum_{n=0}^{\infty} H_n(x) H_n(x') \frac{z^n}{n!} &= \sum_{n=0}^{\infty} H_n(x) \frac{1}{\sqrt{\pi} n!} \int_{-\infty}^{\infty} du \, (-2\mathrm{i}uz)^n \exp\bigl(-(u - \mathrm{i}x')^2\bigr) \\ &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} du \, \exp\bigl(-4\mathrm{i}xuz + 4u^2 z^2\bigr) \exp\bigl(-(u - \mathrm{i}x')^2\bigr) \\ &= \frac{1}{\sqrt{1 - 4z^2}} \exp\left(-4z \frac{z\,(x^2 + x'^2) - xx'}{1 - 4z^2}\right).\end{aligned} \tag{D.7}$$

This requires $|z| < 1/2$ for convergence. In Sections 6.3 and 13.1 we need this in the form for $|z| < 1$,

$$\begin{aligned}&\sum_{n=0}^{\infty} H_n(x) H_n(x') \frac{z^n}{2^n n!} \exp\left(-\frac{x^2 + x'^2}{2}\right) \\ &= \frac{1}{\sqrt{1 - z^2}} \exp\left(-\frac{(1 + z^2)\,(x^2 + x'^2) - 4zxx'}{2\,(1 - z^2)}\right).\end{aligned} \tag{D.8}$$

Indeed, applications of this equation for the harmonic oscillator are usually in the framework of distributions and require the limit $|z| \to 1$. In principle we should therefore replace the corresponding phase factors z in Sections 6.3 and 13.1 with $z \exp(-\epsilon)$, and take the limit $\epsilon \to +0$ after applying any distributions which are derived from (D.8).

[18] F.G. Mehler, J. Math. 66, 161 (1866).

Appendix E: The Baker-Campbell-Hausdorff Formula

The Baker-Campbell-Hausdorff formula explains how to combine the product of exponentials $\exp(A)\cdot\exp(B)$ into a single operator exponential $\exp[\Phi(A,B)]$, if the series expansion for $\Phi(A,B)$ provided by the Baker-Campbell-Hausdorff formula converges.
We try to determine $\Phi(A,B)$ as a power series in a parameter λ,

$$\exp[\lambda A]\cdot\exp[\lambda B]=\exp[\Phi(\lambda A,\lambda B)],\quad \Phi(\lambda A,\lambda B)=\sum_{n=1}^{\infty}\lambda^n c_n(A,B).$$

We also use the notation of the adjoint action of an operator A on an operator B,

$$A^{(ad)}\circ B=-[A,B].$$

We start with

$$\exp[\alpha A]\cdot\exp[\beta B]=\exp[\Phi(\alpha A,\beta B)].$$

This implies with lemma (6.16) the equations

$$\begin{aligned}
B&=\exp[-\Phi(\alpha A,\beta B)]\frac{\partial}{\partial\beta}\exp[\Phi(\alpha A,\beta B)]=\sum_{n=1}^{\infty}\frac{(-)^n}{n!}\ {}^{n}[\Phi(\alpha A,\beta B),\partial_\beta]\\
&=-\sum_{n=1}^{\infty}\frac{(-)^n}{n!}\ {}^{n-1}[\ \Phi(\alpha A,\beta B),\partial_\beta\Phi(\alpha A,\beta B)]\\
&=\sum_{n=1}^{\infty}\frac{1}{n!}\left(\Phi(\alpha A,\beta B)^{(ad)}\right)^{n-1}\circ\partial_\beta\Phi(\alpha A,\beta B)\\
&=\frac{\exp[\Phi(\alpha A,\beta B)^{(ad)}]-1}{\Phi(\alpha A,\beta B)^{(ad)}}\circ\partial_\beta\Phi(\alpha A,\beta B)
\end{aligned}$$

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and

$$
\begin{aligned}
A &= -\exp[\Phi(\alpha A,\beta B)]\frac{\partial}{\partial\alpha}\exp[-\Phi(\alpha A,\beta B)] = -\sum_{n=1}^{\infty}\frac{1}{n!}\,{}^{n}[\Phi(\alpha A,\beta B),\partial_\alpha] \\
&= \sum_{n=1}^{\infty}\frac{1}{n!}\,{}^{n-1}[\,\Phi(\alpha A,\beta B),\partial_\alpha\Phi(\alpha A,\beta B)] \\
&= \sum_{n=1}^{\infty}\frac{1}{n!}\left(-\Phi(\alpha A,\beta B)^{(ad)}\right)^{n-1}\circ\partial_\alpha\Phi(\alpha A,\beta B) \\
&= \frac{1-\exp[-\Phi(\alpha A,\beta B)^{(ad)}]}{\Phi(\alpha A,\beta B)^{(ad)}}\circ\partial_\alpha\Phi(\alpha A,\beta B).
\end{aligned}
$$

For the inversion of these equations, we notice

$$
\begin{aligned}
\left(\frac{\exp(z)-1}{z}\right)^{-1} &= \frac{z}{\exp(z)-1} = z\frac{\exp(-z/2)}{\exp(z/2)-\exp(-z/2)} \\
&= \frac{z}{2}\frac{\exp(z/2)+\exp(-z/2)}{\exp(z/2)-\exp(-z/2)} - \frac{z}{2} \\
&= \frac{z}{2}\coth\frac{z}{2} - \frac{z}{2} = 1 + \sum_{n=1}^{\infty}\frac{(-)^{n+1}}{(2n)!}B_n z^{2n} - \frac{z}{2}, \\
\left(\frac{1-\exp(-z)}{z}\right)^{-1} &= \frac{z}{1-\exp(-z)} = z\frac{\exp(z/2)}{\exp(z/2)-\exp(-z/2)} \\
&= \frac{z}{2}\frac{\exp(z/2)+\exp(-z/2)}{\exp(z/2)-\exp(-z/2)} + \frac{z}{2} \\
&= \frac{z}{2}\coth\frac{z}{2} + \frac{z}{2} = 1 + \sum_{n=1}^{\infty}\frac{(-)^{n+1}}{(2n)!}B_n z^{2n} + \frac{z}{2},
\end{aligned}
$$

where the coefficients B_n are Bernoulli numbers.
The previous equations yield (with $\Phi(\alpha A,\beta B)^{(ad)}\circ A = -[\Phi(\alpha A,\beta B),A]$)

$$
\begin{aligned}
\partial_\alpha\Phi(\alpha A,\beta B) &= \frac{\Phi(\alpha A,\beta B)^{(ad)}}{2}\coth\frac{\Phi(\alpha A,\beta B)^{(ad)}}{2}\circ A \\
&\quad -\frac{1}{2}[\Phi(\alpha A,\beta B),A], \\
\partial_\beta\Phi(\alpha A,\beta B) &= \frac{\Phi(\alpha A,\beta B)^{(ad)}}{2}\coth\frac{\Phi(\alpha A,\beta B)^{(ad)}}{2}\circ B \\
&\quad +\frac{1}{2}[\Phi(\alpha A,\beta B),B], \\
\partial_\lambda\Phi(\lambda A,\lambda B) &= \Big[\partial_\alpha\Phi(\alpha A,\beta B)+\partial_\beta\Phi(\alpha A,\beta B)\Big]_{\alpha=\beta=\lambda} \\
&= \frac{\Phi(\lambda A,\lambda B)^{(ad)}}{2}\coth\frac{\Phi(\lambda A,\lambda B)^{(ad)}}{2}\circ(A+B) \\
&\quad +\frac{1}{2}[A-B,\Phi(\lambda A,\lambda B)],
\end{aligned}
$$

i.e.

$$\partial_\lambda \Phi(\lambda A, \lambda B) = A + B + \sum_{n=1}^{\infty} \frac{(-)^{n+1}}{(2n)!} B_n \cdot [\Phi(\lambda A, \lambda B)^{(ad)}]^{2n} \circ (A + B) + \frac{1}{2}[A - B, \Phi(\lambda A, \lambda B)]. \tag{E.1}$$

Equation (E.1) provides us with a recursion relation for the nth order coefficient functions $c_n(A, B)$,

$$(n+1)c_{n+1}(A,B) = \frac{1}{2}[A - B, c_n(A,B)] + \sum_{m=1}^{[n/2]} \frac{(-)^{m+1}}{(2m)!} B_m \times \sum_{\substack{1 \le k_1, k_2, \ldots k_{2m} \\ k_1 + \ldots + k_{2m} = n}} [c_{k_{2m}}(A,B), [\ldots, [c_{k_2}(A,B), [c_{k_1}(A,B), A + B]] \ldots]], \tag{E.2}$$

with

$$c_0(A,B) = 0, \quad c_1(A,B) = A + B.$$

This yields

$$c_2(A,B) = \frac{1}{2}[A,B],$$

$$\begin{aligned} c_3(A,B) &= \frac{1}{12}[A - B, [A,B]] + \frac{1}{6} B_1 [A + B, [A + B, A + B]] \\ &= \frac{1}{12}[A,[A,B]] + \frac{1}{12}[B,[B,A]], \end{aligned}$$

$$\begin{aligned} c_4(A,B) &= \frac{1}{96}[A - B, [A,[A,B]] + [B,[B,A]]] \\ &\quad + \frac{1}{16} B_1 [A + B, [[A,B], A + B]] \\ &= \frac{1}{96}\Big([A,[A,[A,B]]] - [B,[B,[B,A]]] + [A,[B,[B,A]]] \\ &\quad - [B,[A,[A,B]]] - [A,[A,[A,B]]] + [B,[B,[B,A]]] \\ &\quad + [A,[B,[B,A]]] - [B,[A,[A,B]]] \Big) \\ &= \frac{1}{48}[A,[B,[B,A]]] - \frac{1}{48}[B,[A,[A,B]]] = \frac{1}{24}[A,[B,[B,A]]]. \end{aligned}$$

The Jacobi identity

$$[A,[B,C]] + [B,[C,A]] + [C,[A,B]] = 0$$

was used in the last step for c_4.

Appendix F: The Logarithm of a Matrix

Exponentials of square matrices $\underline{G}$, $\underline{M} = \exp \underline{G} = \sum_{n=0}^{\infty} \underline{G}^n/n!$, are frequently used for the representation of symmetry transformations. Indeed, the properties of continuous symmetry transformations are often discussed in terms of their first order approximations $\underline{1} + \underline{G}$, where it is assumed that continuity of the symmetries allows for parameter choices such that $\max |G_{ij}| \ll 1$. It is therefore of interest that the logarithm $\underline{G} = \ln \underline{M}$ of invertible square matrices can also be defined, although the existence of $\underline{G}$ does not imply that it can be chosen to satisfy $\max |G_{ij}| \ll 1$ for $\underline{M}$ close to the unit matrix, see below.
Suppose $\underline{M}$ is a complex invertible square matrix which is related to its Jordan canonical form through

$$\underline{M} = \underline{T} \cdot \oplus_n \underline{J}_n \cdot \underline{T}^{-1}.$$

Each of the smaller square matrices $\underline{J}_n$ has the form

$$\underline{J} = \lambda \underline{1} \tag{F.1}$$

or the form

$$\underline{J} = \begin{pmatrix} \lambda & 1 & 0 & 0 & \dots & 0 & 0 & 0 \\ 0 & \lambda & 1 & 0 & \dots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & \lambda & 1 & 0 \\ 0 & 0 & 0 & 0 & \dots & 0 & \lambda & 1 \\ 0 & 0 & 0 & 0 & \dots & 0 & 0 & \lambda \end{pmatrix}, \tag{F.2}$$

and $\det(\underline{M}) \neq 0$ implies that none of the eigenvalues λ can vanish.
In the case (F.1) we have

$$\underline{J} = \exp(\ln \lambda \underline{1}), \quad \ln \underline{J} = \ln \lambda \underline{1}.$$

However, it is also possible to construct the logarithm of a Jordan block matrix (F.2). The direct sum of the logarithms of all the matrices $\underline{J}_n$ then yields the logarithm of the matrix $\underline{M}$,

$$\underline{M} = \exp(\underline{T} \cdot \oplus_n \ln \underline{J}_n \cdot \underline{T}^{-1}), \quad \ln \underline{M} = \underline{T} \cdot \oplus_n \ln \underline{J}_n \cdot \underline{T}^{-1}.$$

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Suppose the Jordan matrix (F.2) is a $(\nu+1)\times(\nu+1)$ matrix. We define $(\nu+1)\times(\nu+1)$ matrices $\underline{N}_n$, $0\le n\le\nu$, according to $(\underline{N}_n)_{ij}=\delta_{i+n,j}$, i.e. $\underline{N}_0$ is the $(\nu+1)\times(\nu+1)$ unit matrix and $\underline{N}_{1\le n\le\nu}$ has non-vanishing entries 1 only in the nth diagonal above the main diagonal. These matrices satisfy the multiplication law $\underline{N}_m\cdot\underline{N}_n=\Theta(\nu-m-n+\epsilon)\underline{N}_{m+n}$, which also implies $\underline{N}_n=(\underline{N}_1)^n$.
Each $(\nu+1)\times(\nu+1)$ Jordan block can be written as $\underline{J}=\lambda\underline{N}_0+\underline{N}_1$, and its logarithm can be defined through

$$\begin{aligned}\underline{X}=\ln\underline{J}&=\begin{pmatrix}\ln\lambda & \lambda^{-1} & -\lambda^{-2}/2 & \lambda^{-3}/3 & \dots & (-)^{\nu-1}\lambda^{-\nu}/\nu\\ 0 & \ln\lambda & \lambda^{-1} & -\lambda^{-2}/2 & \dots & (-)^{\nu-2}\lambda^{-(\nu-1)}/(\nu-1)\\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots\\ 0 & 0 & 0 & 0 & \dots & -\lambda^{-2}/2\\ 0 & 0 & 0 & 0 & \dots & \lambda^{-1}\\ 0 & 0 & 0 & 0 & \dots & \ln\lambda\end{pmatrix}\\ &=\underline{N}_0\ln\lambda-\sum_{n=1}^{\nu}\frac{(-\lambda)^{-n}}{n}\underline{N}_n.\end{aligned}\tag{F.3}$$

We can prove $\exp(\underline{X})=\underline{J}$ in the following way. The N-th power of $\underline{X}$ is (here $0<\epsilon<1$ is introduced to avoid the ambiguity of the Θ function at 0)

$$\begin{aligned}\underline{X}^N=&\,\underline{N}_0(\ln\lambda)^N+(-)^N\sum_{1\le n_1,n_2\dots n_N}^{\nu+1-N}\Theta\left(\nu+\epsilon-\sum_{i=1}^{N}n_i\right)\\ &\times\frac{(-\lambda)^{-n_1-n_2-\dots-n_N}}{n_1\cdot n_2\cdot\ldots\cdot n_N}\underline{N}_{n_1+n_2+\dots+n_N}.\\ &-(-)^N N\ln\lambda\sum_{1\le n_1,n_2\dots n_{N-1}}^{\nu+2-N}\Theta\left(\nu+\epsilon-\sum_{i=1}^{N-1}n_i\right)\\ &\times\frac{(-\lambda)^{-n_1-n_2-\dots-n_{N-1}}}{n_1\cdot n_2\cdot\ldots\cdot n_{N-1}}\underline{N}_{n_1+n_2+\dots+n_{N-1}}\\ &+(-)^N\binom{N}{2}(\ln\lambda)^2\\ &\times\sum_{1\le n_1,n_2\dots n_{N-2}}^{\nu+3-N}\Theta\left(\nu+\epsilon-\sum_{i=1}^{N-2}n_i\right)\\ &\times\frac{(-\lambda)^{-n_1-n_2-\dots-n_{N-2}}}{n_1\cdot n_2\cdot\ldots\cdot n_{N-2}}\underline{N}_{n_1+n_2+\dots+n_{N-2}}+\dots\\ &-N(\ln\lambda)^{N-1}\sum_{n=1}^{\nu}\frac{(-\lambda)^{-n}}{n}\underline{N}_n.\end{aligned}$$

We can combine terms in the form

$$\begin{aligned}\underline{X}^N &= \underline{N}_0(\ln\lambda)^N + \sum_{m=1}^{N}(-)^m\binom{N}{m}(\ln\lambda)^{N-m}\\ &\quad\times\sum_{1\le n_1,n_2\ldots n_m}^{\nu+1-m}\Theta\left(\nu+\epsilon-\sum_{i=1}^{m}n_i\right)\frac{(-\lambda)^{-n_1-n_2-\ldots-n_m}}{n_1\cdot n_2\cdot\ldots\cdot n_m}\underline{N}_{n_1+n_2+\ldots+n_m}\\ &= \underline{N}_0(\ln\lambda)^N + \sum_{M=1}^{\nu}(-\lambda)^{-M}\underline{N}_M\sum_{m=1}^{\min(N,M)}(-)^m\binom{N}{m}(\ln\lambda)^{N-m}\\ &\quad\times\sum_{\substack{1\le n_1,n_2\ldots n_m\\ n_1+n_2+\ldots+n_m=M}}^{M+1-m}\frac{1}{n_1\cdot n_2\cdot\ldots\cdot n_m}.\end{aligned}$$

This is after isolation of the term with $M=1$ in the sum,

$$\begin{aligned}\underline{X}^N &= \underline{N}_0(\ln\lambda)^N + N\frac{(\ln\lambda)^{N-1}}{\lambda}\underline{N}_1+\Theta(\nu-2+\epsilon)\\ &\quad\times\sum_{M=2}^{\nu}(-\lambda)^{-M}\underline{N}_M\left(\sum_{m=1}^{\min(N,M)}(-)^m\binom{N}{m}(\ln\lambda)^{N-m}\right.\\ &\quad\left.\times\sum_{\substack{1\le n_1,n_2\ldots n_m\\ n_1+n_2+\ldots+n_m=M}}^{M+1-m}\frac{1}{n_1\cdot n_2\cdot\ldots\cdot n_m}\right).\end{aligned}$$

Only the first two terms survive in

$$\exp(\underline{X}) = \underline{1}+\sum_{N=1}^{\infty}\frac{X^N}{N!} = \lambda\underline{N}_0+\underline{N}_1 = \underline{J}$$

because the sum over N in the term of order M reduces to

$$\sum_{N=m}^{\infty}\frac{(\ln\lambda)^{N-m}}{(N-m)!} = \lambda,$$

and the remaining sums yield for $M\ge 1$

$$\begin{aligned}&\sum_{m=1}^{M}\frac{(-)^m}{m!}\sum_{\substack{1\le n_1,n_2\ldots n_m\\ n_1+n_2+\ldots+n_m=M}}^{M+1-m}\frac{1}{n_1\cdot n_2\cdot\ldots\cdot n_m}\\ &= \frac{1}{2\pi\mathrm{i}}\oint_{|z|<1}dz\sum_{m=1}^{M}\frac{(-)^m}{m!}\sum_{n_1,n_2\ldots n_m=1}^{\infty}\frac{z^{n_1+n_2+\ldots+n_m-M-1}}{n_1\cdot n_2\cdot\ldots\cdot n_m}\\ &= \frac{1}{2\pi\mathrm{i}}\oint_{|z|<1}dz\sum_{m=1}^{\infty}\frac{(-)^m}{m!}\sum_{n_1,n_2\ldots n_m=1}^{\infty}\frac{z^{n_1+n_2+\ldots+n_m-M-1}}{n_1\cdot n_2\cdot\ldots\cdot n_m}\end{aligned}$$

$$= \frac{1}{2\pi \mathrm{i}} \oint_{|z|<1} dz \sum_{m=1}^{\infty} \frac{(-)^m}{m!} \left(\sum_{n=1}^{\infty} \frac{z^n}{n} \right)^m z^{-M-1}$$

$$= \frac{1}{2\pi \mathrm{i}} \oint_{|z|<1} dz \sum_{m=1}^{\infty} \frac{[\ln(1-z)]^m}{m!} z^{-M-1}$$

$$= \frac{1}{2\pi \mathrm{i}} \oint_{|z|<1} dz \big(z^{-M-1} - z^{-M} \big) = -\delta_{M,1}.$$

Equation (F.3) is a special case of a general procedure to define functions $\underline{M} \to f(\underline{M})$ of square matrices [14], and for every $n \in \mathbb{Z}$, the matrix $\underline{X} + 2\pi \mathrm{i} n \underline{N}_0$ is also a logarithm of $\underline{J}$.

A glance at (F.3) tells us that we should avoid matrices with Jordan blocks in their eigenvalue decomposition if we want to find logarithms with the property $\max |(\ln \underline{M})_{ij}| \ll 1$ for $\max |M_{ij} - \delta_{ij}| \ll 1$. This can be achieved if we use hermitian and unitary matrices, and if $\underline{M}$ does not satisfy this condition, we can use its polar decomposition

$$\underline{M} = \underline{H} \cdot \underline{U} = (\underline{M} \cdot \underline{M}^+)^{1/2} \cdot [(\underline{M} \cdot \underline{M}^+)^{-1/2} \cdot \underline{M}] \tag{F.4}$$

in terms of a hermitian and a unitary factor, or a symmetric and an orthogonal factor if $\underline{M}$ is real. The factors will then have logarithms with small matrix elements if $\underline{M}$ is close to the unit matrix, i.e. the analysis of continuous symmetries in finite-dimensional vector spaces eventually requires the analysis of up to two first order transformations $\underline{1} + \ln \underline{H}$ and $\underline{1} + \ln \underline{U}$. This is the case e.g. for Lorentz transformations, where $\underline{H}$ is the pure boost part and $\underline{U}$ is the rotation.

Appendix G: Dirac γ matrices

It is useful for the understanding and explicit construction of γ matrices to discuss their properties in a general number d of spacetime dimensions. γ matrices in more than four spacetime dimensions are regularly used in theories which hypothesize the existence of extra spacetime dimensions. On the other hand, variants of the Dirac equation in two space dimensions or three spacetime dimensions have also become relevant in materials science for the description of electrons in Graphene.

γ-matrices in d dimensions

The condition (21.28), $\{\gamma_\mu, \gamma_\nu\} = -2\eta_{\mu\nu}$, implies that any product of n gamma coefficients $\gamma_\alpha \cdot \gamma_\beta \cdot \ldots \cdot \gamma_\omega$ can be reduced to a product of $n-2$ coefficients if two indices have the same value. We can also re-order any product such that the indices have increasing values. These observations imply that the d coefficients γ_μ can produce at most 2^d linearly independent combinations

$$\mathbf{1},\ \gamma_0,\ \gamma_1,\ \ldots,\ \gamma_{d-1},\ \gamma_0 \cdot \gamma_1,\ \gamma_0 \cdot \gamma_2,\ \ldots,\ \gamma_0 \cdot \gamma_1 \cdot \ldots \cdot \gamma_{d-1}. \tag{G.1}$$

We are actually interested in matrix representations of the algebra generated by (21.28), and consider the coefficients γ^μ and the objects in (G.1) as matrices in the following. We first discuss the case that d is an *even number of spacetime dimensions*, and we define multi-indices J through

$$\Gamma_J = \gamma_{\mu_1} \cdot \gamma_{\mu_2} \cdot \ldots \cdot \gamma_{\mu_n}, \quad \mu_1 < \mu_2 < \ldots < \mu_n, \quad n(J) = n. \tag{G.2}$$

It is easy to prove that

$$\mathrm{tr}(\Gamma_J) = 0. \tag{G.3}$$

For even $n(J)$ this follows from the anti-commutativity of the γ-matrices and the cyclic invariance of the trace. For odd $n(J)$ this follows from the fact that there is at least one γ-matrix not contained in Γ_J, e.g. γ_1, and therefore

$$\mathrm{tr}(\Gamma_J) = -\mathrm{tr}(\gamma_1^2 \cdot \Gamma_J) = -\mathrm{tr}(\gamma_1 \cdot \Gamma_J \cdot \gamma_1) = \mathrm{tr}(\gamma_1^2 \cdot \Gamma_J) = -\mathrm{tr}(\Gamma_J) = 0.$$

The product $\Gamma_I \cdot \Gamma_J$ reduces either to a Γ-matrix Γ_K if $I \neq J$, or otherwise

$$\Gamma_I^2 = \pm\mathbf{1},$$

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and this implies orthogonality of all the Γ-matrices and $\mathbf{1}$,

$$\mathrm{tr}(\Gamma_I \cdot \Gamma_J) \propto \delta_{IJ}.$$

For *even number of spacetime dimensions* d this implies that all the 2^d matrices in (G.1) are indeed linearly independent, and therefore a minimal matrix representation of (21.28) requires at least $(2^{d/2} \times 2^{d/2})$-matrices. We will see by explicit construction that such a representation exists, and because $2^{d/2}$ is the minimal dimension, the representation must be irreducible, i.e. cannot split into smaller matrices acting in spaces of lower dimensions. The representation also turns out to be unique up to similarity transformations

$$\gamma_\mu \to \gamma'_\mu = A \cdot \gamma_\mu \cdot A^{-1}.$$

For *odd number of spacetime dimensions* d, we also define the matrices Γ_J according to (G.1), but now the previous proof of $\mathrm{tr}(\Gamma_J) = 0$ only goes through for all the matrices Γ_J *except for the last matrix in the list*,

$$\Gamma_{0,1,\dots d-1} = \gamma_0 \cdot \gamma_1 \cdot \ldots \cdot \gamma_{d-1}.$$

For odd d, this matrix contains an odd number of γ-matrices, and it contains all γ-matrices, such that the previous proof of vanishing trace for odd $n(J)$ does not go through for this particular matrix. Furthermore, this matrix has the properties

$$[\Gamma_{0,1,\dots d-1}, \Gamma_J] = 0, \tag{G.4}$$

$$\Gamma^2_{0,1,\dots d-1} = (-)^{(d+2)(d-1)/2}\mathbf{1} = (-)^{(d-1)/2}\mathbf{1}. \tag{G.5}$$

Commutativity with all other matrices implies that in every irreducible representation

$$\Gamma_{0,1,\dots d-1} = \pm(-)^{(d-1)/4}\mathbf{1}, \tag{G.6}$$

see the following subsection for the proof.
This also implies that every product Γ_J of $n(J) \geq (d+1)/2$ γ matrices is up to a numerical factor a product Γ_I of $n(I) = d - n(J) \leq (d-1)/2$ γ matrices,

$$\begin{aligned}\Big[\Gamma_J\Big]_{n(J)\geq(d+1)/2} &= \Big[\mathbf{1}\cdot\Gamma_J\Big]_{n(J)\geq(d+1)/2} \propto \Big[\Gamma_{0,1,\dots d-1}\cdot\Gamma_J\Big]_{n(J)\geq(d+1)/2} \\ &\propto \Big[\Gamma_I\Big]_{n(I)\leq(d-1)/2}.\end{aligned}$$

Therefore there are only 2^{d-1} linearly independent matrices in (G.1) for odd d, and the minimal possible dimension of the representation is only $2^{(d-1)/2}$. The explicit construction later on confirms that the minimal dimension also works for odd number of spacetime dimensions. There are two different equivalence classes of matrix representations with dimension $2^{(d-1)/2}$.

Proof that in irreducible representations $\Gamma_{0,1,\dots d-1} \propto \mathbf{1}$ for odd spacetime dimension d

$\Gamma_{0,1,\dots d-1}$ commutes with all Γ_J. Suppose that we have an irreducible matrix representation of (G.1) in a vector space V of dimension $\dim V$. If λ is an eigenvalue of $\Gamma_{0,1,\dots d-1} \propto \mathbf{1}$,

$$\det(\Gamma_{0,1,\dots d-1} - \lambda\mathbf{1}) = 0,$$

we have

$$\dim\Big((\Gamma_{0,1,\dots d-1} - \lambda\mathbf{1})\cdot V\Big) \leq \dim V - 1,$$

and

$$\Gamma_J \cdot (\Gamma_{0,1,\dots d-1} - \lambda\mathbf{1})\cdot V = (\Gamma_{0,1,\dots d-1} - \lambda\mathbf{1})\cdot \Gamma_J \cdot V.$$

The last equation would imply that $(\Gamma_{0,1,\dots d-1} - \lambda\mathbf{1})\cdot V$, if non-empty, would be an invariant subspace under the action of the γ-matrices, in contradiction to the irreducibility of V. Therefore we must have

$$(\Gamma_{0,1,\dots d-1} - \lambda\mathbf{1})\cdot V = \emptyset, \quad \Gamma_{0,1,\dots d-1} = \lambda\mathbf{1}$$

in every irreducible representation. Equation (G.5) tells us that

$$\lambda = \pm(-)^{(d-1)/4}.$$

The proof is simply an adaption of the proof of Schur's lemma from group theory.

Recursive construction of γ-matrices in different dimensions

We will use the following conventions for the explicit construction of γ-matrices: Up to similarity transformations, the γ-matrices in *two spacetime dimensions* are

$$\gamma_0 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \gamma_1 = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \tag{G.7}$$

For the recursive construction in higher dimensions $d \geq 3$ we now assume that γ_μ, $0 \leq \mu \leq d-2$, are γ-matrices in $d-1$ dimensions.
For the construction of γ-matrices in an *odd number d of spacetime dimensions* there are two inequivalent choices,

$$\Gamma_0 = \pm \mathrm{i}^{(d-3)/2}\gamma_0\gamma_1\dots\gamma_{d-2} = \pm \begin{pmatrix} -\underline{1} & 0 \\ 0 & \underline{1} \end{pmatrix}, \quad \Gamma_i = \gamma_i, \quad 1 \leq i \leq d-2,$$
$$\Gamma_{d-1} = -\mathrm{i}\gamma_0. \tag{G.8}$$

For the construction of γ-matrices in an *even number* $d \geq 4$ *of spacetime dimensions* there is only one equivalence class of representations,

$$\Gamma_0 = \begin{pmatrix} 0 & \underline{1} \\ \underline{1} & 0 \end{pmatrix}, \quad \Gamma_i = \begin{pmatrix} 0 & -\gamma_0\gamma_i \\ \gamma_0\gamma_i & 0 \end{pmatrix}, \quad 1 \leq i \leq d-2,$$
$$\Gamma_{d-1} = \begin{pmatrix} 0 & -\gamma_0 \\ \gamma_0 & 0 \end{pmatrix}. \tag{G.9}$$

Note that it does not matter from which of the two possible representations $\pm\gamma_0$ in the odd number $d-1$ of lower dimensions we start since Γ_0 intertwines the two possibilities,

$$\Gamma_0\Gamma_i\Gamma_0 = -\Gamma_i, \quad 1 \leq i \leq d-1.$$

The possibility of similarity transformations implies that there are infinitely many equivalent possibilities to construct these bases of γ-matrices. The construction described here was motivated from the desire to have Weyl bases (i.e. all γ^μ have only off-diagonal non-vanishing $(2^{(d/2)-1} \times 2^{(d/2)-1})$ blocks) in even dimensions, and to have the next best solution, viz. Dirac bases (i.e. $\gamma^0 = \pm\mathrm{diag}(\underline{1}, -\underline{1})$, all γ^i like in a Weyl basis), in odd dimensions. Note that all the representations (G.8) and (G.9) of the γ-matrices in odd or even dimensions fulfill

$$\gamma_0^+ = \gamma_0, \quad \gamma_i^+ = -\gamma_i,$$

or equivalently

$$\gamma_\mu^+ = \gamma_0\gamma_\mu\gamma_0. \tag{G.10}$$

Every set of γ-matrices is equivalent to a set satisfying equation (G.10). We will prove this in the following subsection.

Proof that every set of γ-matrices is equivalent to a set which satisfies equation (G.10)

In this section we do not use summation convention, but spell out all summations explicitly.
We define $2^{[d/2]} \times 2^{[d/2]}$ matrices $X_0 = \gamma_0$, $X_i = \mathrm{i}\gamma_i$,

$$\{X_\mu, X_\nu\} = 2\delta_{\mu\nu}$$

and prove that the matrices X_μ are equivalent to a set of unitary matrices Y_μ. Since the matrices Y_μ also satisfy $Y_\mu^{-1} = Y_\mu$, unitarity also implies hermiticity of Y_μ. We use the abbreviation $N = 2^{[d/2]}$, and consider the set $\mathbb{S}$ of $N \times N$ matrices

$$\mathbf{1}, \quad X_I = X_{\mu_1} \cdot \ldots \cdot X_{\mu_n}, \quad n \leq \hat{n} = \begin{cases} d, & d \text{ even} \\ \frac{d-1}{2}, & d \text{ odd} \end{cases}$$

This set does not form a group, but only a group modulo $\mathbb{Z}_2$. But this is sufficient for the standard argument for equivalence to a set of unitary matrices. The $N \times N$ matrix

$$H = \mathbf{1} + \sum_I X_I^+ \cdot X_I = H^+$$

is invariant under right translations in the set $\mathbb{S}$ (i.e. right multiplication of all elements by some fixed element Z), because that just permutes the elements, up to possible additional minus signs which cancel in H,

$$H = Z^+ \cdot Z + \sum_I (X_I \cdot Z)^+ \cdot (X_I \cdot Z).$$

H also has N positive eigenvalues, because

$$H \cdot \psi_\alpha = h_\alpha \psi_\alpha, \quad \psi_\alpha^+ \cdot \psi_\beta = \delta_{\alpha\beta}, \tag{G.11}$$

implies

$$h_\alpha = \psi_\alpha^+ \cdot H \cdot \psi_\alpha = 1 + \sum_I |X_I \cdot \psi_\alpha|^2 > 0. \tag{G.12}$$

If we define the matrix Ψ with columns ψ_α, equations (G.11) and (G.12) imply

$$\mathrm{diag}(h_1, \ldots h_N) = \Psi^+ \cdot H \cdot \Psi, \quad H = \Psi \cdot \mathrm{diag}(h_1, \ldots h_N) \cdot \Psi^+.$$

Now define

$$Y_\mu = \Psi \cdot \mathrm{diag}(\sqrt{h_1}, \ldots \sqrt{h_N}) \cdot \Psi^+ \cdot X_\mu \cdot (\Psi \cdot \mathrm{diag}(\sqrt{h_1}, \ldots \sqrt{h_N}) \cdot \Psi^+)^{-1}.$$

These matrices are indeed unitary,

$$\begin{aligned}
Y_\mu^+ \cdot Y_\mu &= \left(\Psi \cdot \mathrm{diag}\left(\sqrt{h_1}, \ldots \sqrt{h_N}\right) \cdot \Psi^+\right)^{-1} \cdot X_\mu^+ \\
&\quad \times \left(\Psi \cdot \mathrm{diag}\left(\sqrt{h_1}, \ldots \sqrt{h_N}\right) \cdot \Psi^+\right)^{2} \cdot X_\mu \\
&\quad \times \left(\Psi \cdot \mathrm{diag}\left(\sqrt{h_1}, \ldots \sqrt{h_N}\right) \cdot \Psi^+\right)^{-1} \\
&= \left(\Psi \cdot \mathrm{diag}\left(\sqrt{h_1}, \ldots \sqrt{h_N}\right) \cdot \Psi^+\right)^{-1} \cdot X_\mu^+ \cdot H \cdot X_\mu \\
&\quad \times \left(\Psi \cdot \mathrm{diag}\left(\sqrt{h_1}, \ldots \sqrt{h_N}\right) \cdot \Psi^+\right)^{-1} \\
&= \left(\Psi \cdot \mathrm{diag}\left(\sqrt{h_1}, \ldots \sqrt{h_N}\right) \cdot \Psi^+\right)^{-1} \\
&\quad \times [X_\mu^+ \cdot X_\mu + \textstyle\sum_I (Z_I \cdot X_\mu)^+ \cdot (Z_I \cdot X_\mu)] \\
&\quad \times \left(\Psi \cdot \mathrm{diag}\left(\sqrt{h_1}, \ldots \sqrt{h_N}\right) \cdot \Psi^+\right)^{-1} \\
&= \left(\Psi \cdot \mathrm{diag}\left(\sqrt{h_1}, \ldots \sqrt{h_N}\right) \cdot \Psi^+\right)^{-1} \cdot H \\
&\quad \times \left(\Psi \cdot \mathrm{diag}\left(\sqrt{h_1}, \ldots \sqrt{h_N}\right) \cdot \Psi^+\right)^{-1} = \mathbf{1},
\end{aligned}$$

which concludes the proof of equivalence of the matrices X_μ to a set of matrices Y_μ which are both unitary and hermitian.
Equivalence of the γ matrices to hermitian or anti-hermitian matrices also implies that every reducible representation of γ matrices is fully reducible.

Uniqueness theorem for γ matrices

Every irreducible matrix representation of the algebra generated by (21.28) is equivalent to one of the representations constructed in the previous section.
We first consider the case of *even number of dimensions d*. The theorem says that in this case every irreducible matrix representation of (21.28) is equivalent to the representation in terms of $2^{d/2} \times 2^{d/2}$ constructed in equation (G.9).
Proof: Suppose the $N_1 \times N_1$ matrices $\gamma_{1,\mu}$ and the $N_2 \times N_2$ matrices $\gamma_{2,\mu}$, $0 \leq \mu \leq d-1$, are two sets of matrices which satisfy the conditions (21.28). V_1 is the N_1-dimensional vector space in which the matrices $\gamma_{1,\mu}$ act. We use the representations from the previous section, equation (G.9), for the matrices $\gamma_{2,\mu}$. This implies $N_1 \geq N_2 = 2^{d/2}$.
We denote the components of the matrices $\gamma_{1,\mu}$ and $\gamma_{2,\mu}$ with ${\gamma_{1,\mu}}^a{}_b$ and ${\gamma_{2,\mu}}^\alpha{}_\beta$, respectively, and define again multi-indices J for the two sets of γ matrices (cf. equation (G.2)),

$$\Gamma_{r,J} = \gamma_{r,\mu_1} \cdot \gamma_{r,\mu_2} \cdot \ldots \cdot \gamma_{r,\mu_n}, \ 1 \leq r \leq 2, \ \mu_1 < \mu_2 < \ldots < \mu_n, \ n(J) = n.$$

The squares of these matrices satisfy

$${\Gamma_{r,I}}^2 = \pm \mathbf{1} = s_I \mathbf{1}, \tag{G.13}$$

where the sign factor

$$s_I = (-)^{n(I)[n(I)+1]/2} \eta_{\mu_1\mu_1} \tag{G.14}$$

arises as the product of the factor $(-)^{n(I)[n(I)-1]/2}$ from the permutations of γ matrices times a factor $(-)^{n(I)}$ from the sign on the right hand side of (21.28). Only $\eta_{\mu_1\mu_1}$ appears on the right hand side of (G.14) because we have only one timelike direction. For the case of general spacetime signature one could simply include the product $\eta_{\mu_1\mu_1}\eta_{\mu_2\mu_2}\ldots\eta_{\mu_n\mu_n}$.
The results from the previous section for even d tell us that a set $\Gamma_{r,I}$ with fixed r, after augmentation with the $N_r \times N_r$ unit matrix $\Gamma_{r,0} = \mathbf{1}$, contains 2^d linearly independent matrices.
We define the $N_1 \cdot N_2$ different $N_1 \times N_2$ matrices ${E_a}^\alpha$ with components

$$({E_a}^\alpha)^b{}_\beta = {\delta_a}^b {\delta^\alpha}_\beta.$$

We use these matrices to form the $N_1 \times N_2$ matrices

$${\Omega_a}^\alpha = {E_a}^\alpha + \sum_J s_J \Gamma_{1,J} \cdot {E_a}^\alpha \cdot \Gamma_{2,J},$$

i.e. in components,

$$(\Omega_a{}^\alpha)^b{}_\beta = \delta_a{}^b\delta^\alpha{}_\beta + \sum_J s_J(\Gamma_{1,J})^b{}_a(\Gamma_{2,J})^\alpha{}_\beta. \tag{G.15}$$

Suppose $I \neq J$. The conditions (21.28) imply that there is always a multi-index $K \neq I$ such that

$$\Gamma_{r,I}\cdot\Gamma_{r,J} = \pm\Gamma_{r,K},$$

and inversion of this equation yields

$$s_I s_J \Gamma_{r,J}\cdot\Gamma_{r,I} = \pm s_K\Gamma_{r,K}.$$

This implies

$$\begin{aligned}
\Gamma_{1,I}\cdot\Omega_a{}^\alpha &= \Gamma_{1,I}\cdot E_a{}^\alpha + E_a{}^\alpha\cdot\Gamma_{2,I} + \sum_{J\neq I} s_J\Gamma_{1,I}\cdot\Gamma_{1,J}\cdot E_a{}^\alpha\cdot\Gamma_{2,J} \\
&= \left(s_I\Gamma_{1,I}\cdot E_a{}^\alpha\cdot\Gamma_{2,I} + E_a{}^\alpha + \sum_{J\neq I} s_I s_J\Gamma_{1,I}\cdot\Gamma_{1,J}\cdot E_a{}^\alpha\cdot\Gamma_{2,J}\cdot\Gamma_{2,I}\right) \\
&\quad\times\Gamma_{2,I} \\
&= \left(s_I\Gamma_{1,I}\cdot E_a{}^\alpha\cdot\Gamma_{2,I} + E_a{}^\alpha + \sum_{K\neq I} s_K\Gamma_{1,K}\cdot E_a{}^\alpha\cdot\Gamma_{2,K}\right)\cdot\Gamma_{2,I} \\
&= \Omega_a{}^\alpha\cdot\Gamma_{2,I}.
\end{aligned} \tag{G.16}$$

We know that the matrices (G.15) are not null matrices, $\Omega_a{}^\alpha \neq \mathbf{0}$, because we know that the 2^d matrices $\{\mathbf{1}, \Gamma_{2,J}\}$ are linearly independent,

$$\delta_a{}^b\mathbf{1} + \sum_J s_J(\Gamma_{1,J})^b{}_a\Gamma_{2,J} \neq 0.$$

This implies that the N_1-dimensional vector space V_1 with basis vectors $\boldsymbol{e}_{1,b}$, $1 \leq b \leq N_1$, contains non-vanishing sets of $N_2 = 2^{d/2} \leq N_1$ basis vectors

$$\boldsymbol{e}_{1,\beta} = \boldsymbol{e}_{1,b}(\Omega_a{}^\alpha)^b{}_\beta, \quad 1 \leq \beta \leq 2^{d/2} \leq N_1,$$

which are invariant under the action of the γ matrices,

$$\boldsymbol{e}_{1,b}(\gamma_{1,\mu})^b{}_c(\Omega_a{}^\alpha)^c{}_\delta = \boldsymbol{e}_{1,b}(\Omega_a{}^\alpha)^b{}_\beta(\gamma_{2,\mu})^\beta{}_\delta.$$

Therefore the representation of γ matrices in V_1 is either reducible into invariant subspaces of dimension $2^{d/2}$, or we have $N_1 = 2^{d/2}$. In the latter case we must have

$$\det(\Omega_a{}^\alpha) \neq 0,$$

because representations spaces of dimension $2^{d/2}$ are irreducible, and therefore

$$\gamma_{1,\mu} = \Omega_a{}^\alpha\cdot\gamma_{2,\mu}\cdot(\Omega_a{}^\alpha)^{-1}$$

is equivalent to the representation from the previous section for even d. Thus concludes the proof for even d.
For *odd* d we observe that the matrices γ_μ, $0 \le \mu \le d-2$, form a set of γ matrices for a $(d-1)$-dimensional Minkowski space, which according to the previous result is either reducible or equivalent to the corresponding representation (G.9) from the previous section. However, using those matrices, the missing matrix γ_{d-1} can easily be constructed according to the prescription

$$\gamma_{d-1} = \pm(-)^{(d-1)(d-2)/4}\gamma_0 \cdot \gamma_1 \cdot \ldots \cdot \gamma_{d-2}. \tag{G.17}$$

Now assume that the matrices γ_μ, $0 \le \mu \le d-2$, are $2^{(d-1)/2} \times 2^{(d-1)/2}$ matrices, i.e. they form an *irreducible* representation of γ matrices for a $(d-1)$-dimensional Minkowski space. In that case completeness of the set

$$\Gamma_J = \gamma_{\mu_1} \cdot \gamma_{\mu_2} \cdot \ldots \cdot \gamma_{\mu_n}, \quad 0 \le \mu_1 < \mu_2 < \ldots < \mu_n \le d-2 \tag{G.18}$$

in $GL(2^{(d-1)/2})$ implies that (G.17) are the only options for the construction of γ_{d-1}. Completeness of the set (G.18) also implies that the two options for the sign in (G.17) correspond to two inequivalent representations.
On the other hand, if the matrices γ_μ, $0 \le \mu \le d-2$, form a *reducible* representation of γ matrices for a $(d-1)$-dimensional Minkowski space, they must be equivalent to matrices with irreducible $2^{(d-1)/2} \times 2^{(d-1)/2}$ matrices $\hat{\gamma}_\mu$, $0 \le \mu \le d-2$, in diagonal blocks. Then one can easily prove from the anti-commutation relations and the completeness of the set

$$\hat{\Gamma}_J = \hat{\gamma}_{\mu_1} \cdot \hat{\gamma}_{\mu_2} \cdot \ldots \cdot \hat{\gamma}_{\mu_n}, \quad 0 \le \mu_1 < \mu_2 < \ldots < \mu_n \le d-2$$

in $2^{(d-1)/2}$-dimensional subspaces, that the matrix γ_{d-1} must consist of $2^{(d-1)/2} \times 2^{(d-1)/2}$ blocks which are proportional to $\hat{\gamma}_0 \cdot \hat{\gamma}_1 \cdot \ldots \cdot \hat{\gamma}_{d-2}$. The property ${\gamma_{d-1}}^2 = -\mathbf{1}$ can then be used to demonstrate that γ_{d-1} must be equivalent to a matrix which only has matrices

$$\hat{\gamma}_{d-1} = \pm(-)^{(d-1)(d-2)/4}\hat{\gamma}_0 \cdot \hat{\gamma}_1 \cdot \ldots \cdot \hat{\gamma}_{d-2}$$

in diagonal $2^{(d-1)/2} \times 2^{(d-1)/2}$ blocks, i.e. a representation of γ matrices for odd number d of dimensions is either equivalent to one of the two irreducible $2^{(d-1)/2}$-dimensional representations distinguished by the sign in (G.17), or it is a reducible representation.
In the recursive construction of γ matrices described above, I separated the two equivalence classes of irreducible representations through the sign of γ_0 instead of γ_{d-1}, cf. (G.8). We can cast the sign from γ_{d-1} to γ_0 through the similarity transformation

$$\gamma_0 \;\to\; \gamma_0 \cdot \gamma_{d-1} \cdot \gamma_0 \cdot \gamma_0 \cdot \gamma_{d-1} = -\gamma_0,$$

$$\gamma_{d-1} \;\to\; \gamma_0 \cdot \gamma_{d-1} \cdot \gamma_{d-1} \cdot \gamma_0 \cdot \gamma_{d-1} = -\gamma_{d-1},$$

$$\gamma_i \;\to\; \gamma_0 \cdot \gamma_{d-1} \cdot \gamma_i \cdot \gamma_0 \cdot \gamma_{d-1} = \gamma_i, \quad 1 \le i \le d-2.$$

Contraction and trace theorems for γ matrices

Here we explicitly refer of four spacetime dimensions again. The generalizations to any number of spacetime dimensions are trivial.
Equation (21.28) implies

$$\gamma^\sigma\gamma_\sigma = -4.$$

The higher order contraction theorems then follow from (21.28) and application of the next lower order contraction theorem, e.g.

$$\gamma^\sigma\gamma^\mu\gamma_\sigma = \{\gamma^\sigma,\gamma^\mu\}\gamma_\sigma - \gamma^\mu\gamma^\sigma\gamma_\sigma = 2\gamma^\mu,$$

$$\gamma^\sigma\gamma^\mu\gamma^\nu\gamma_\sigma = 4\eta^{\mu\nu}, \quad \gamma^\sigma\gamma^\mu\gamma^\nu\gamma^\rho\gamma_\sigma = 2\gamma^\rho\gamma^\nu\gamma^\mu.$$

The trace of a product of an odd number of γ matrices vanishes. The trace of a product of two γ matrices is determined by their basic anti-commutation property,

$$\mathrm{tr}(\gamma_\mu\gamma_\nu) = -4\eta_{\mu\nu}.$$

The trace of a product of four γ matrices is easily evaluated using their anti-commutation properties and cyclic invariance of the trace

$$\begin{aligned}\mathrm{tr}(\gamma_\kappa\gamma_\lambda\gamma_\mu\gamma_\nu) &= 8\eta_{\kappa\lambda}\eta_{\mu\nu} - \mathrm{tr}(\gamma_\kappa\gamma_\lambda\gamma_\nu\gamma_\mu) = 8\eta_{\kappa\lambda}\eta_{\mu\nu} - \mathrm{tr}(\gamma_\mu\gamma_\kappa\gamma_\lambda\gamma_\nu)\\ &= 8\eta_{\kappa\lambda}\eta_{\mu\nu} - 8\eta_{\mu\kappa}\eta_{\lambda\nu} + \mathrm{tr}(\gamma_\kappa\gamma_\mu\gamma_\lambda\gamma_\nu)\\ &= 8\eta_{\kappa\lambda}\eta_{\mu\nu} - 8\eta_{\mu\kappa}\eta_{\lambda\nu} + 8\eta_{\mu\lambda}\eta_{\kappa\nu} - \mathrm{tr}(\gamma_\kappa\gamma_\lambda\gamma_\mu\gamma_\nu)\,,\end{aligned}$$

i.e.

$$\mathrm{tr}(\gamma_\kappa\gamma_\lambda\gamma_\mu\gamma_\nu) = 4\eta_{\kappa\lambda}\eta_{\mu\nu} - 4\eta_{\mu\kappa}\eta_{\lambda\nu} + 4\eta_{\mu\lambda}\eta_{\kappa\nu}. \tag{G.19}$$

For yet higher orders we observe

$$\begin{aligned}\mathrm{tr}(\gamma_{\alpha_1}\dots\gamma_{\alpha_{2n}}\gamma_\mu\gamma_\nu) &= -2\eta_{\mu\nu}\mathrm{tr}(\gamma_{\alpha_1}\dots\gamma_{\alpha_{2n}}) - \mathrm{tr}(\gamma_\mu\gamma_{\alpha_1}\dots\gamma_{\alpha_{2n}}\gamma_\nu)\\ &= -2\eta_{\mu\nu}\mathrm{tr}(\gamma_{\alpha_1}\dots\gamma_{\alpha_{2n}}) + \mathrm{tr}(\gamma_{\alpha_1}\gamma_\mu\gamma_{\alpha_2}\dots\gamma_{\alpha_{2n}}\gamma_\nu)\\ &\quad +2\eta_{\mu\alpha_1}\mathrm{tr}(\gamma_{\alpha_2}\dots\gamma_{\alpha_{2n}}\gamma_\nu)\\ &= -2\eta_{\mu\nu}\mathrm{tr}(\gamma_{\alpha_1}\dots\gamma_{\alpha_{2n}}) - \mathrm{tr}(\gamma_{\alpha_1}\dots\gamma_{\alpha_{2n}}\gamma_\mu\gamma_\nu)\\ &\quad -2\sum_{i=1}^{2n}(-)^i\eta_{\mu\alpha_i}\mathrm{tr}\big(\gamma_{\alpha_1}\dots\gamma_{\alpha_{i-1}}\gamma_{\alpha_{i+1}}\dots\gamma_{\alpha_{2n}}\gamma_\nu\big)\,,\end{aligned}$$

i.e. we have a recursion relation

$$\begin{aligned}\mathrm{tr}(\gamma_{\alpha_1}\dots\gamma_{\alpha_{2n}}\gamma_\mu\gamma_\nu) &= -\eta_{\mu\nu}\mathrm{tr}(\gamma_{\alpha_1}\dots\gamma_{\alpha_{2n}})\\ &\quad -\sum_{i=1}^{2n}(-)^i\eta_{\mu\alpha_i}\mathrm{tr}\big(\gamma_{\alpha_1}\dots\gamma_{\alpha_{i-1}}\gamma_{\alpha_{i+1}}\dots\gamma_{\alpha_{2n}}\gamma_\nu\big)\,.\end{aligned}$$

This yields for products of six γ matrices

$$\begin{aligned}\mathrm{tr}(\gamma_\rho\gamma_\sigma\gamma_\kappa\gamma_\lambda\gamma_\mu\gamma_\nu) = &-4\eta_{\rho\sigma}\eta_{\kappa\lambda}\eta_{\mu\nu} + 4\eta_{\rho\kappa}\eta_{\sigma\lambda}\eta_{\mu\nu} - 4\eta_{\rho\lambda}\eta_{\kappa\sigma}\eta_{\mu\nu} + 4\eta_{\sigma\kappa}\eta_{\lambda\nu}\eta_{\mu\rho}\\ &-4\eta_{\sigma\lambda}\eta_{\kappa\nu}\eta_{\mu\rho} + 4\eta_{\sigma\nu}\eta_{\lambda\kappa}\eta_{\mu\rho} - 4\eta_{\rho\kappa}\eta_{\lambda\nu}\eta_{\mu\sigma} + 4\eta_{\rho\lambda}\eta_{\kappa\nu}\eta_{\mu\sigma}\\ &-4\eta_{\rho\nu}\eta_{\lambda\kappa}\eta_{\mu\sigma} + 4\eta_{\rho\sigma}\eta_{\lambda\nu}\eta_{\mu\kappa} - 4\eta_{\rho\lambda}\eta_{\sigma\nu}\eta_{\mu\kappa} + 4\eta_{\rho\nu}\eta_{\lambda\sigma}\eta_{\mu\kappa}\\ &-4\eta_{\rho\sigma}\eta_{\kappa\nu}\eta_{\mu\lambda} + 4\eta_{\rho\kappa}\eta_{\sigma\nu}\eta_{\mu\lambda} - 4\eta_{\rho\nu}\eta_{\kappa\sigma}\eta_{\mu\lambda}, \end{aligned} \tag{G.20}$$

and the trace of the product of eight γ matrices contains 105 terms,

$$\begin{aligned}&\mathrm{tr}(\gamma_\alpha\gamma_\beta\gamma_\rho\gamma_\sigma\gamma_\kappa\gamma_\lambda\gamma_\mu\gamma_\nu) = 4\eta_{\rho\sigma}\eta_{\kappa\lambda}\eta_{\mu\nu}\eta_{\alpha\beta} - 4\eta_{\rho\kappa}\eta_{\sigma\lambda}\eta_{\mu\nu}\eta_{\alpha\beta} + 4\eta_{\rho\lambda}\eta_{\kappa\sigma}\eta_{\mu\nu}\eta_{\alpha\beta}\\
&-4\eta_{\sigma\kappa}\eta_{\lambda\nu}\eta_{\mu\rho}\eta_{\alpha\beta} + 4\eta_{\sigma\lambda}\eta_{\kappa\nu}\eta_{\mu\rho}\eta_{\alpha\beta} - 4\eta_{\sigma\nu}\eta_{\lambda\kappa}\eta_{\mu\rho}\eta_{\alpha\beta} + 4\eta_{\rho\kappa}\eta_{\lambda\nu}\eta_{\mu\sigma}\eta_{\alpha\beta}\\
&-4\eta_{\rho\lambda}\eta_{\kappa\nu}\eta_{\mu\sigma}\eta_{\alpha\beta} + 4\eta_{\rho\nu}\eta_{\lambda\kappa}\eta_{\mu\sigma}\eta_{\alpha\beta} - 4\eta_{\rho\sigma}\eta_{\lambda\nu}\eta_{\mu\kappa}\eta_{\alpha\beta} + 4\eta_{\rho\lambda}\eta_{\sigma\nu}\eta_{\mu\kappa}\eta_{\alpha\beta}\\
&-4\eta_{\rho\nu}\eta_{\lambda\sigma}\eta_{\mu\kappa}\eta_{\alpha\beta} + 4\eta_{\rho\sigma}\eta_{\kappa\nu}\eta_{\mu\lambda}\eta_{\alpha\beta} - 4\eta_{\rho\kappa}\eta_{\sigma\nu}\eta_{\mu\lambda}\eta_{\alpha\beta} + 4\eta_{\rho\nu}\eta_{\kappa\sigma}\eta_{\mu\lambda}\eta_{\alpha\beta}\\
&-4\eta_{\sigma\kappa}\eta_{\lambda\mu}\eta_{\nu\beta}\eta_{\alpha\rho} + 4\eta_{\sigma\lambda}\eta_{\kappa\mu}\eta_{\nu\beta}\eta_{\alpha\rho} - 4\eta_{\sigma\mu}\eta_{\lambda\kappa}\eta_{\nu\beta}\eta_{\alpha\rho} + 4\eta_{\kappa\lambda}\eta_{\mu\beta}\eta_{\nu\sigma}\eta_{\alpha\rho}\\
&-4\eta_{\kappa\mu}\eta_{\lambda\beta}\eta_{\nu\sigma}\eta_{\alpha\rho} + 4\eta_{\kappa\beta}\eta_{\mu\lambda}\eta_{\nu\sigma}\eta_{\alpha\rho} - 4\eta_{\sigma\lambda}\eta_{\mu\beta}\eta_{\nu\kappa}\eta_{\alpha\rho} + 4\eta_{\sigma\mu}\eta_{\lambda\beta}\eta_{\nu\kappa}\eta_{\alpha\rho}\\
&-4\eta_{\sigma\beta}\eta_{\mu\lambda}\eta_{\nu\kappa}\eta_{\alpha\rho} + 4\eta_{\sigma\kappa}\eta_{\mu\beta}\eta_{\nu\lambda}\eta_{\alpha\rho} - 4\eta_{\sigma\mu}\eta_{\kappa\beta}\eta_{\nu\lambda}\eta_{\alpha\rho} + 4\eta_{\sigma\beta}\eta_{\mu\kappa}\eta_{\nu\lambda}\eta_{\alpha\rho}\\
&-4\eta_{\sigma\kappa}\eta_{\lambda\beta}\eta_{\nu\mu}\eta_{\alpha\rho} + 4\eta_{\sigma\lambda}\eta_{\kappa\beta}\eta_{\nu\mu}\eta_{\alpha\rho} - 4\eta_{\sigma\beta}\eta_{\lambda\kappa}\eta_{\nu\mu}\eta_{\alpha\rho} + 4\eta_{\rho\kappa}\eta_{\lambda\mu}\eta_{\nu\beta}\eta_{\alpha\sigma}\\
&-4\eta_{\rho\lambda}\eta_{\kappa\mu}\eta_{\nu\beta}\eta_{\alpha\sigma} + 4\eta_{\rho\mu}\eta_{\lambda\kappa}\eta_{\nu\beta}\eta_{\alpha\sigma} - 4\eta_{\kappa\lambda}\eta_{\mu\beta}\eta_{\nu\rho}\eta_{\alpha\sigma} + 4\eta_{\kappa\mu}\eta_{\lambda\beta}\eta_{\nu\rho}\eta_{\alpha\sigma}\\
&-4\eta_{\kappa\beta}\eta_{\mu\lambda}\eta_{\nu\rho}\eta_{\alpha\sigma} + 4\eta_{\rho\lambda}\eta_{\mu\beta}\eta_{\nu\kappa}\eta_{\alpha\sigma} - 4\eta_{\rho\mu}\eta_{\lambda\beta}\eta_{\nu\kappa}\eta_{\alpha\sigma} + 4\eta_{\rho\beta}\eta_{\mu\lambda}\eta_{\nu\kappa}\eta_{\alpha\sigma}\\
&-4\eta_{\rho\kappa}\eta_{\mu\beta}\eta_{\nu\lambda}\eta_{\alpha\sigma} + 4\eta_{\rho\mu}\eta_{\kappa\beta}\eta_{\nu\lambda}\eta_{\alpha\sigma} - 4\eta_{\rho\beta}\eta_{\mu\kappa}\eta_{\nu\lambda}\eta_{\alpha\sigma} + 4\eta_{\rho\kappa}\eta_{\lambda\beta}\eta_{\nu\mu}\eta_{\alpha\sigma}\\
&-4\eta_{\rho\lambda}\eta_{\kappa\beta}\eta_{\nu\mu}\eta_{\alpha\sigma} + 4\eta_{\rho\beta}\eta_{\lambda\kappa}\eta_{\nu\mu}\eta_{\alpha\sigma} - 4\eta_{\rho\sigma}\eta_{\lambda\mu}\eta_{\nu\beta}\eta_{\alpha\kappa} + 4\eta_{\rho\lambda}\eta_{\sigma\mu}\eta_{\nu\beta}\eta_{\alpha\kappa}\\
&-4\eta_{\rho\mu}\eta_{\lambda\sigma}\eta_{\nu\beta}\eta_{\alpha\kappa} + 4\eta_{\sigma\lambda}\eta_{\mu\beta}\eta_{\nu\rho}\eta_{\alpha\kappa} - 4\eta_{\sigma\mu}\eta_{\lambda\beta}\eta_{\nu\rho}\eta_{\alpha\kappa} + 4\eta_{\sigma\beta}\eta_{\mu\lambda}\eta_{\nu\rho}\eta_{\alpha\kappa}\\
&-4\eta_{\rho\lambda}\eta_{\mu\beta}\eta_{\nu\sigma}\eta_{\alpha\kappa} + 4\eta_{\rho\mu}\eta_{\lambda\beta}\eta_{\nu\sigma}\eta_{\alpha\kappa} - 4\eta_{\rho\beta}\eta_{\mu\lambda}\eta_{\nu\sigma}\eta_{\alpha\kappa} + 4\eta_{\rho\sigma}\eta_{\mu\beta}\eta_{\nu\lambda}\eta_{\alpha\kappa}\\
&-4\eta_{\rho\mu}\eta_{\sigma\beta}\eta_{\nu\lambda}\eta_{\alpha\kappa} + 4\eta_{\rho\beta}\eta_{\mu\sigma}\eta_{\nu\lambda}\eta_{\alpha\kappa} - 4\eta_{\rho\sigma}\eta_{\lambda\beta}\eta_{\nu\mu}\eta_{\alpha\kappa} + 4\eta_{\rho\lambda}\eta_{\sigma\beta}\eta_{\nu\mu}\eta_{\alpha\kappa}\\
&-4\eta_{\rho\beta}\eta_{\lambda\sigma}\eta_{\nu\mu}\eta_{\alpha\kappa} + 4\eta_{\rho\sigma}\eta_{\kappa\mu}\eta_{\nu\beta}\eta_{\alpha\lambda} - 4\eta_{\rho\kappa}\eta_{\sigma\mu}\eta_{\nu\beta}\eta_{\alpha\lambda} + 4\eta_{\rho\mu}\eta_{\kappa\sigma}\eta_{\nu\beta}\eta_{\alpha\lambda}\\
&-4\eta_{\sigma\kappa}\eta_{\mu\beta}\eta_{\nu\rho}\eta_{\alpha\lambda} + 4\eta_{\sigma\mu}\eta_{\kappa\beta}\eta_{\nu\rho}\eta_{\alpha\lambda} - 4\eta_{\sigma\beta}\eta_{\mu\kappa}\eta_{\nu\rho}\eta_{\alpha\lambda} + 4\eta_{\rho\kappa}\eta_{\mu\beta}\eta_{\nu\sigma}\eta_{\alpha\lambda}\\
&-4\eta_{\rho\mu}\eta_{\kappa\beta}\eta_{\nu\sigma}\eta_{\alpha\lambda} + 4\eta_{\rho\beta}\eta_{\mu\kappa}\eta_{\nu\sigma}\eta_{\alpha\lambda} - 4\eta_{\rho\sigma}\eta_{\mu\beta}\eta_{\nu\kappa}\eta_{\alpha\lambda} + 4\eta_{\rho\mu}\eta_{\sigma\beta}\eta_{\nu\kappa}\eta_{\alpha\lambda}\\
&-4\eta_{\rho\beta}\eta_{\mu\sigma}\eta_{\nu\kappa}\eta_{\alpha\lambda} + 4\eta_{\rho\sigma}\eta_{\kappa\beta}\eta_{\nu\mu}\eta_{\alpha\lambda} - 4\eta_{\rho\kappa}\eta_{\sigma\beta}\eta_{\nu\mu}\eta_{\alpha\lambda} + 4\eta_{\rho\beta}\eta_{\kappa\sigma}\eta_{\nu\mu}\eta_{\alpha\lambda}\\
&-4\eta_{\rho\sigma}\eta_{\kappa\lambda}\eta_{\nu\beta}\eta_{\alpha\mu} + 4\eta_{\rho\kappa}\eta_{\sigma\lambda}\eta_{\nu\beta}\eta_{\alpha\mu} - 4\eta_{\rho\lambda}\eta_{\kappa\sigma}\eta_{\nu\beta}\eta_{\alpha\mu} + 4\eta_{\sigma\kappa}\eta_{\lambda\beta}\eta_{\nu\rho}\eta_{\alpha\mu}\\
&-4\eta_{\sigma\lambda}\eta_{\kappa\beta}\eta_{\nu\rho}\eta_{\alpha\mu} + 4\eta_{\sigma\beta}\eta_{\lambda\kappa}\eta_{\nu\rho}\eta_{\alpha\mu} - 4\eta_{\rho\kappa}\eta_{\lambda\beta}\eta_{\nu\sigma}\eta_{\alpha\mu} + 4\eta_{\rho\lambda}\eta_{\kappa\beta}\eta_{\nu\sigma}\eta_{\alpha\mu}\\
&-4\eta_{\rho\beta}\eta_{\lambda\kappa}\eta_{\nu\sigma}\eta_{\alpha\mu} + 4\eta_{\rho\sigma}\eta_{\lambda\beta}\eta_{\nu\kappa}\eta_{\alpha\mu} - 4\eta_{\rho\lambda}\eta_{\sigma\beta}\eta_{\nu\kappa}\eta_{\alpha\mu} + 4\eta_{\rho\beta}\eta_{\lambda\sigma}\eta_{\nu\kappa}\eta_{\alpha\mu}\\
&-4\eta_{\rho\sigma}\eta_{\kappa\beta}\eta_{\nu\lambda}\eta_{\alpha\mu} + 4\eta_{\rho\kappa}\eta_{\sigma\beta}\eta_{\nu\lambda}\eta_{\alpha\mu} - 4\eta_{\rho\beta}\eta_{\kappa\sigma}\eta_{\nu\lambda}\eta_{\alpha\mu} + 4\eta_{\rho\sigma}\eta_{\kappa\lambda}\eta_{\mu\beta}\eta_{\alpha\nu}\\
&-4\eta_{\rho\kappa}\eta_{\sigma\lambda}\eta_{\mu\beta}\eta_{\alpha\nu} + 4\eta_{\rho\lambda}\eta_{\kappa\sigma}\eta_{\mu\beta}\eta_{\alpha\nu} - 4\eta_{\sigma\kappa}\eta_{\lambda\beta}\eta_{\mu\rho}\eta_{\alpha\nu} + 4\eta_{\sigma\lambda}\eta_{\kappa\beta}\eta_{\mu\rho}\eta_{\alpha\nu}\\
&-4\eta_{\sigma\beta}\eta_{\lambda\kappa}\eta_{\mu\rho}\eta_{\alpha\nu} + 4\eta_{\rho\kappa}\eta_{\lambda\beta}\eta_{\mu\sigma}\eta_{\alpha\nu} - 4\eta_{\rho\lambda}\eta_{\kappa\beta}\eta_{\mu\sigma}\eta_{\alpha\nu} + 4\eta_{\rho\beta}\eta_{\lambda\kappa}\eta_{\mu\sigma}\eta_{\alpha\nu}\\
&-4\eta_{\rho\sigma}\eta_{\lambda\beta}\eta_{\mu\kappa}\eta_{\alpha\nu} + 4\eta_{\rho\lambda}\eta_{\sigma\beta}\eta_{\mu\kappa}\eta_{\alpha\nu} - 4\eta_{\rho\beta}\eta_{\lambda\sigma}\eta_{\mu\kappa}\eta_{\alpha\nu} + 4\eta_{\rho\sigma}\eta_{\kappa\beta}\eta_{\mu\lambda}\eta_{\alpha\nu}\\
&-4\eta_{\rho\kappa}\eta_{\sigma\beta}\eta_{\mu\lambda}\eta_{\alpha\nu} + 4\eta_{\rho\beta}\eta_{\kappa\sigma}\eta_{\mu\lambda}\eta_{\alpha\nu}. \end{aligned} \tag{G.21}$$

Appendix H: Spinor representations of the Lorentz group

The explicit form of the Lagrange density (21.50) for the Dirac field and the appearance of the factor $\overline{\Psi} = \Psi^+ \cdot \gamma^0$ are determined by the requirement of Lorentz invariance of $\mathcal{L}$ and the transformation properties of spinors under Lorentz transformations. However, before we can elaborate on these points, we have to revisit the Lorentz transformation (B.8), which is also denoted as the vector representation because it acts on spacetime vectors. We can discuss this in general numbers n of spatial dimensions and $d = n + 1$ of spacetime dimensions.

Generators of proper orthochronous Lorentz transformations in the vector and spinor representations

We can write the two factors of a proper orthochronous Lorentz transformation (B.8) as exponentials of Lie algebra elements,

$$\Lambda(\boldsymbol{u}, \underline{\epsilon}) = \Lambda(\boldsymbol{u}) \cdot \Lambda(\underline{\epsilon}) = \exp(\boldsymbol{u} \cdot \boldsymbol{K}) \cdot \exp\left(\frac{1}{2}\epsilon^{ij} L_{ij}\right). \tag{H.1}$$

For the boost part we use explicit construction to prove that every proper Lorentz boost can be written in the form $\exp(\boldsymbol{u} \cdot \boldsymbol{K})$.
For the rotation part we can use the general result that every element of a compact Lie group can be written as a single exponential of a corresponding Lie algebra element, or we can use the fact that a general $n \times n$ rotation matrix consists of n orthonormal row vectors, which fixes the general form in terms of $n(n-1)/2$ parameters, and then demonstrate that the $n(n-1)/2$ parameters ϵ^{ij} of $\exp(\epsilon^{ij} L_{ij}/2)$ provide a general parametrization of n orthonormal row vectors.
Alternatively, we can consider (H.1) as an example for the polar decomposition (F.4) and infer the representation in terms of matrix exponentials from the results on matrix logarithms in Appendix F.
The boost part is

$$\Lambda(\boldsymbol{u}) = \exp(\boldsymbol{u} \cdot \boldsymbol{K}) = \exp\left(\epsilon^{i0} L_{i0}\right) = \exp\left(\mathrm{i}\epsilon^{i0} M_{i0}\right) \tag{H.2}$$

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and the spatial rotation is

$$\Lambda(\underline{\epsilon}) = \exp\left(\frac{1}{2}\epsilon^{ij}L_{ij}\right) = \exp\left(\frac{\mathrm{i}}{2}\epsilon^{ij}M_{ij}\right), \tag{H.3}$$

where ϵ_{ij} is the rotation angle in the ij plane. The generators are (in the vector representation),

$$(L_{\mu\nu})^{\rho}{}_{\sigma} = \mathrm{i}\,(M_{\mu\nu})^{\rho}{}_{\sigma} = (\eta^{\rho}{}_{\mu}\eta_{\nu\sigma} - \eta^{\rho}{}_{\nu}\eta_{\mu\sigma})\,. \tag{H.4}$$

These matrices generate the Lie algebra $\mathrm{so}(1, d-1)$,

$$\begin{aligned}[L_{\mu\nu}, L_{\rho\sigma}] &= \eta_{\nu\rho}L_{\mu\sigma} + \eta_{\mu\sigma}L_{\nu\rho} - \eta_{\mu\rho}L_{\nu\sigma} - \eta_{\nu\sigma}L_{\mu\rho} \\ &= -(L_{\mu\nu})_{\rho}{}^{\lambda}L_{\lambda\sigma} - (L_{\mu\nu})_{\sigma}{}^{\lambda}L_{\rho\lambda}.\end{aligned} \tag{H.5}$$

In 4-dimensional Minkowski space, the angles ϵ_{ij} are related to the rotation angles φ_i around the x^i-axis according to

$$\varphi_i = \frac{1}{2}\epsilon_{ijk}\epsilon_{jk}, \quad \epsilon_{ij} = \epsilon_{ijk}\varphi_k. \tag{H.6}$$

To see how the boost vector $\boldsymbol{u}$ is related to the velocity $\boldsymbol{v} = c\boldsymbol{\beta}$, we will explicitly calculate the boost matrix $\Lambda(\boldsymbol{u})$. We have with a contravariant row index and a covariant column index, as in (B.8),

$$\boldsymbol{u}\cdot\boldsymbol{K} = u^i L_{i0} = \mathrm{i}u^i M_{i0} = \begin{pmatrix} 0 & -u_1 & \dots & -u_{d-1} \\ -u_1 & 0 & \dots & 0 \\ \vdots & \vdots & & \vdots \\ -u_{d-1} & 0 & \dots & 0 \end{pmatrix} = \begin{pmatrix} 0 & -\boldsymbol{u}^T \\ -\boldsymbol{u} & \underline{0} \end{pmatrix},$$

$$(\boldsymbol{u}\cdot\boldsymbol{K})^2 = \begin{pmatrix} \boldsymbol{u}^2 & \boldsymbol{0}^T \\ \boldsymbol{0} & \boldsymbol{u}\otimes\boldsymbol{u}^T \end{pmatrix}, \quad (\boldsymbol{u}\cdot\boldsymbol{K})^{2n} = u^{2n}\begin{pmatrix} 1 & \boldsymbol{0}^T \\ \boldsymbol{0} & \hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T \end{pmatrix}, \tag{H.7}$$

$$(\boldsymbol{u}\cdot\boldsymbol{K})^{2n+1} = u^{2n+1}\begin{pmatrix} 0 & -\hat{\boldsymbol{u}}^T \\ -\hat{\boldsymbol{u}} & \underline{0} \end{pmatrix}. \tag{H.8}$$

For the interpretation of the $(d-1)\times(d-1)$ matrices $\hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T$ and $\underline{1} - \hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T$, note that for every $(d-1)$-dimensional spatial vector $\boldsymbol{r}$

$$\boldsymbol{r}_{\parallel} = \hat{\boldsymbol{u}}(\hat{\boldsymbol{u}}^T\cdot\boldsymbol{r}) = (\hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T)\cdot\boldsymbol{r}$$

is the part $\boldsymbol{r}_{\parallel}$ of the vector which is parallel to $\boldsymbol{u}$, and

$$\boldsymbol{r}_{\perp} = \boldsymbol{r} - \boldsymbol{r}_{\parallel} = (\underline{1} - \hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T)\cdot\boldsymbol{r}$$

is the part of the vector which is orthogonal to $\boldsymbol{u}$.
Substitution of the results (H.7,H.8) into (H.2) yields for the boost in the direction $\hat{\boldsymbol{u}} = \hat{\boldsymbol{\beta}}$

$$\begin{aligned}\Lambda(\boldsymbol{u}) &= \begin{pmatrix} \cosh(u) & \boldsymbol{0}^T \\ \boldsymbol{0} & \underline{1} + \hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T(\cosh(u)-1) \end{pmatrix} + \sinh(u)\begin{pmatrix} 0 & -\hat{\boldsymbol{u}}^T \\ -\hat{\boldsymbol{u}} & \underline{0} \end{pmatrix} \\ &= \begin{pmatrix} \gamma & -\gamma\boldsymbol{\beta}^T \\ -\gamma\boldsymbol{\beta} & \underline{1} - \hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T + \gamma\hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T \end{pmatrix},\end{aligned}$$

i.e.

$$\gamma = \cosh(u), \quad \beta = \tanh(u), \quad u = \operatorname{artanh}(\beta) = \frac{1}{2}\ln\left(\frac{1+\beta}{1-\beta}\right).$$

It may also be worthwhile to write down the corresponding rotation matrix in 4-dimensional Minkowski space. If we introduce the 3×3 matrices for the spatial subsections of the rotation matrices L_{mn},

$$(L_i)_{jk} = \frac{1}{2}\epsilon_{imn}(L_{mn})_{jk} = \epsilon_{ijk},$$

the rotation matrices take the following form,

$$\Lambda(\underline{\epsilon}) = \exp\begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \boldsymbol{\varphi}\cdot\boldsymbol{L} \end{pmatrix} = \begin{pmatrix} 1 & \mathbf{0}^T \\ \mathbf{0} & \exp(\boldsymbol{\varphi}\cdot\boldsymbol{L}) \end{pmatrix},$$

with the 3×3 rotation matrix

$$\exp(\boldsymbol{\varphi}\cdot\boldsymbol{L}) = \hat{\boldsymbol{\varphi}} \otimes \hat{\boldsymbol{\varphi}}^T + \left(\underline{1} - \hat{\boldsymbol{\varphi}} \otimes \hat{\boldsymbol{\varphi}}^T\right)\cos(\varphi) + \hat{\boldsymbol{\varphi}}\cdot\boldsymbol{L}\sin(\varphi).$$

Application of the matrix $\hat{\boldsymbol{\varphi}}\cdot\boldsymbol{L}$ generates a vector product,

$$(\hat{\boldsymbol{\varphi}}\cdot\boldsymbol{L})\cdot\boldsymbol{r} = -\hat{\boldsymbol{\varphi}}\times\boldsymbol{r}.$$

The anticommutation relations (21.28) imply that the properly normalized commutators of γ-matrices,

$$S_{\mu\nu} = \frac{\mathrm{i}}{4}[\gamma_\mu, \gamma_\nu] \tag{H.9}$$

also provide a representation of the Lie algebra so(1,d-1) (H.5),

$$\begin{aligned}[S_{\mu\nu}, S_{\rho\sigma}] &= \mathrm{i}\left(\eta_{\mu\rho}S_{\nu\sigma} + \eta_{\nu\sigma}S_{\mu\rho} - \eta_{\nu\rho}S_{\mu\sigma} - \eta_{\mu\sigma}S_{\nu\rho}\right) \\ &= \mathrm{i}(L_{\mu\nu})_\rho{}^\lambda S_{\lambda\sigma} + \mathrm{i}(L_{\mu\nu})_\sigma{}^\lambda S_{\rho\lambda}.\end{aligned} \tag{H.10}$$

See equations (H.13-H.15) for the proof.
This representation of the Lorentz group is realized in the transformation of Dirac spinors $\psi(x)$ under Lorentz transformations

$$x' = \Lambda(\epsilon)\cdot x = \exp\left(\frac{1}{2}\epsilon^{\mu\nu}L_{\mu\nu}\right)\cdot x,$$

$$\psi'(x') = U(\Lambda)\cdot\psi(x) = \exp\left(\frac{\mathrm{i}}{2}\epsilon^{\mu\nu}S_{\mu\nu}\right)\cdot\psi(x). \tag{H.11}$$

The anticommutation relations (21.28) also imply invariance of the γ-matrices under Lorentz transformations $x' = \Lambda(\epsilon)\cdot x$,

$$\gamma'^\mu = \Lambda^\mu{}_\nu(\epsilon)\exp\left(\frac{\mathrm{i}}{2}\epsilon^{\kappa\lambda}S_{\kappa\lambda}\right)\cdot\gamma^\nu\cdot\exp\left(-\frac{\mathrm{i}}{2}\epsilon^{\rho\sigma}S_{\rho\sigma}\right) = \gamma^\mu, \tag{H.12}$$

see equation (H.16). This invariance property of the γ-matrices also implies form invariance of the Dirac equation under Lorentz transformations,

$$\mathrm{i}\hbar\gamma^\mu\partial'_\mu\psi'(x') - mc\psi'(x') = \exp\left(\frac{\mathrm{i}}{2}\epsilon^{\kappa\lambda}S_{\kappa\lambda}\right)\cdot\left(\mathrm{i}\hbar\gamma^\mu\partial_\mu\psi(x) - mc\psi(x)\right),$$

i.e. *all inertial observers can use the same set of γ-matrices, and the Dirac equation has the same form for all of them.*

Verification of the Lorentz commutation relations for the spinor representations

The anti-commutation relations (21.28) imply

$$\begin{aligned}[\gamma_\mu\gamma_\nu,\gamma_\rho] &= \gamma_\mu\{\gamma_\nu,\gamma_\rho\} - \{\gamma_\mu,\gamma_\rho\}\gamma_\nu = 2\eta_{\mu\rho}\gamma_\nu - 2\eta_{\nu\rho}\gamma_\mu \\ &= 2(L_{\mu\nu})_\rho{}^\sigma\gamma_\sigma, \end{aligned} \tag{H.13}$$

where the matrices $L_{\mu\nu}$ were given in (H.4). Equation (H.13) also implies

$$[S_{\mu\nu},\gamma_\rho] = \mathrm{i}(L_{\mu\nu})_\rho{}^\sigma\gamma_\sigma \tag{H.14}$$

and

$$\begin{aligned}[S_{\mu\nu},S_{\rho\sigma}] &= \frac{\mathrm{i}}{4}[S_{\mu\nu},[\gamma_\rho,\gamma_\sigma]] = \frac{\mathrm{i}}{4}[[S_{\mu\nu},\gamma_\rho],\gamma_\sigma] - \frac{\mathrm{i}}{4}[[S_{\mu\nu},\gamma_\sigma],\gamma_\rho] \\ &= -\frac{1}{4}(L_{\mu\nu})_\rho{}^\lambda[\gamma_\lambda,\gamma_\sigma] + \frac{1}{4}(L_{\mu\nu})_\sigma{}^\lambda[\gamma_\lambda,\gamma_\rho] \\ &= \mathrm{i}(L_{\mu\nu})_\rho{}^\lambda S_{\lambda\sigma} + \mathrm{i}(L_{\mu\nu})_\sigma{}^\lambda S_{\rho\lambda}. \end{aligned} \tag{H.15}$$

Equation (H.14) implies the Lorentz invariance of the γ-matrices,

$$\begin{aligned}\exp\left(\frac{\mathrm{i}}{2}\epsilon^{\mu\nu}S_{\mu\nu}\right)\gamma_\rho\exp\left(-\frac{\mathrm{i}}{2}\epsilon^{\kappa\lambda}S_{\kappa\lambda}\right) &= \left[\exp\left(-\frac{1}{2}\epsilon^{\mu\nu}L_{\mu\nu}\right)\right]_\rho{}^\sigma\gamma_\sigma \\ &= \Lambda^{-1}(\epsilon)_\rho{}^\sigma\gamma_\sigma. \end{aligned} \tag{H.16}$$

Scalar products of spinors and the Lagrangian for the Dirac equation

The hermiticity relation (G.10) implies the following hermiticity property of the Lorentz generators,

$$S^+_{\mu\nu} = \gamma^0 S_{\mu\nu}\gamma^0,$$

and therefore

$$\psi'^+(x') = \psi^+(x)\cdot\gamma^0\exp\left(-\frac{\mathrm{i}}{2}\epsilon^{\mu\nu}S_{\mu\nu}\right)\gamma^0.$$

The adjoint spinor

$$\overline{\psi}(x) = \psi^+(x)\cdot\gamma^0$$

therefore transforms inversely to the spinor $\psi(x)$,

$$\overline{\psi}'(x) = \overline{\psi}(x)\cdot\exp\left(-\frac{\mathrm{i}}{2}\epsilon^{\mu\nu}S_{\mu\nu}\right),$$

and the product of spinors

$$\overline{\psi}(x)\cdot\phi(x) = \psi^+(x)\cdot\gamma^0\cdot\phi(x)$$

is Lorentz invariant. This yields a Lorentz invariant Lagrangian for the Dirac equation,

$$\mathcal{L} = \frac{\mathrm{i}\hbar c}{2}\left(\overline{\psi}(x)\cdot\gamma^\mu\cdot\partial_\mu\psi(x) - \partial_\mu\overline{\psi}(x)\cdot\gamma^\mu\cdot\psi(x)\right) - mc^2\overline{\psi}(x)\cdot\psi(x). \tag{H.17}$$

The spinor representation in the Weyl and Dirac bases of γ-matrices

In *even dimensions*, the construction (G.9) yields γ-matrices of the form

$$\gamma_0 = \begin{pmatrix} 0 & \underline{1} \\ \underline{1} & 0 \end{pmatrix}, \quad \gamma_i = \begin{pmatrix} 0 & \underline{\sigma}_i \\ -\underline{\sigma}_i & 0 \end{pmatrix}, \tag{H.18}$$

with hermitian $(2^{(d/2)-1} \times 2^{(d/2)-1})$ matrices $\underline{\sigma}_i$, which satisfy

$$\{\underline{\sigma}_i, \underline{\sigma}_j\} = 2\delta_{ij}. \tag{H.19}$$

The spinor representation of the Lorentz generators in this Weyl basis is

$$S_{0i} = \frac{\mathrm{i}}{2}\gamma_0\gamma_i = \frac{\mathrm{i}}{2}\begin{pmatrix} -\underline{\sigma}_i & 0 \\ 0 & \underline{\sigma}_i \end{pmatrix}, \quad S_{ij} = \frac{\mathrm{i}}{4}[\gamma_i, \gamma_j] = -\frac{\mathrm{i}}{4}\begin{pmatrix} [\underline{\sigma}_i, \underline{\sigma}_j] & 0 \\ 0 & [\underline{\sigma}_i, \underline{\sigma}_j] \end{pmatrix}.$$

This is the advantage of a Weyl basis: The $2^{d/2}$ components of a spinor explicitly split into two Weyl spinors with $2^{(d/2)-1}$ components. The two Weyl spinors transform separately under proper orthochronous Lorentz transformations. A Dirac spinor representation in even dimensions is therefore reducible under the group of proper orthochronous Lorentz transformations. However, the form of S_{0i} tells us that the two Weyl spinors are transformed into each other under time or space inversions. Therefore the representation of the full Lorentz group really requires the full $2^{d/2}$-dimensional Dirac spinor.
The rotation generators in the Dirac representation in even dimensions are the same as in the Weyl basis, but the boost generators become

$$S_{0i} = -\frac{\mathrm{i}}{2}\begin{pmatrix} 0 & \underline{\sigma}_i \\ \underline{\sigma}_i & 0 \end{pmatrix}.$$

For an *odd number of spacetime dimensions* our construction provides γ-matrices of the form,

$$\gamma_0 = \pm\begin{pmatrix} -\underline{1} & 0 \\ 0 & \underline{1} \end{pmatrix}, \quad \gamma_i = \begin{pmatrix} 0 & \underline{\sigma}_i \\ -\underline{\sigma}_i & 0 \end{pmatrix}, \quad 1 \le i \le d-2,$$

$$\gamma_{d-1} = -\mathrm{i}\begin{pmatrix} 0 & \underline{1} \\ \underline{1} & 0 \end{pmatrix}.$$

The rotation generators $S_{ij}, 1 \le i, j \le d-2$, are the same as in $d-1$ dimensions, but rotations of the $(i, d-1)$ plane are generated by

$$S_{i,d-1} = \frac{1}{2}\begin{pmatrix} \underline{\sigma}_i & 0 \\ 0 & -\underline{\sigma}_i \end{pmatrix},$$

and the boost generators are off-diagonal,

$$S_{0i} = \mp\frac{\mathrm{i}}{2}\begin{pmatrix} 0 & \underline{\sigma}_i \\ \underline{\sigma}_i & 0 \end{pmatrix}, \quad S_{0,d-1} = \pm\frac{1}{2}\begin{pmatrix} 0 & -\underline{1} \\ \underline{1} & 0 \end{pmatrix}.$$

The proper orthochronous Lorentz group therefore mixes all the $2^{(d-1)/2}$ components of a Dirac spinor in odd dimensions.

Reconstruction of the vector representation from the spinor representation

Equation (21.28) implies

$$\mathrm{tr}(\gamma_\mu\gamma_\nu) = -2^{[d/2]}\eta_{\mu\nu}. \tag{H.20}$$

This and the invariance of the γ-matrices (H.12) can be used to reconstruct the vector representation of a proper orthochronous Lorentz transformation from the corresponding spinor representation,

$$\Lambda^\mu{}_\nu(\epsilon) = -2^{-[d/2]}\mathrm{tr}\left[\exp\left(-\frac{\mathrm{i}}{2}\epsilon^{\kappa\lambda}S_{\kappa\lambda}\right)\cdot\gamma^\mu\cdot\exp\left(\frac{\mathrm{i}}{2}\epsilon^{\rho\sigma}S_{\rho\sigma}\right)\cdot\gamma_\nu\right]. \tag{H.21}$$

We can also use equation (H.20) to transform every vector into a spinor of order 2 (or every tensor of order n into a spinor of order $2n$),

$$x(\gamma) = x^\mu\gamma_\mu, \quad x^\mu = -2^{-[d/2]}\mathrm{tr}[\gamma^\mu\cdot x(\gamma)]\,,$$

and the invariance of the γ-matrices implies

$$x'^\mu = \Lambda^\mu{}_\nu(\epsilon)x^\nu \quad\Leftrightarrow\quad x'(\gamma) = \exp\left(\frac{\mathrm{i}}{2}\epsilon^{\kappa\lambda}S_{\kappa\lambda}\right)\cdot x(\gamma)\cdot\exp\left(-\frac{\mathrm{i}}{2}\epsilon^{\rho\sigma}S_{\rho\sigma}\right).$$

Construction of the free Dirac spinors from Dirac spinors at rest

We use $c = 1$ and $d = 4$ in this section. The Dirac equation in momentum space (21.34) is for a Dirac spinor $\psi(E,\mathbf{0})$ at rest

$$(m - E\gamma^0)\psi(E,\mathbf{0}) = 0. \tag{H.22}$$

The hermitian 4×4 matrix γ^0 can only have eigenvalues ±1, which each must be two-fold degenerate because γ^0 is traceless. Therefore Dirac spinors at rest must correspond to energy eigenvalues $E = \pm m$. To construct the free Dirac spinors for arbitrary on-shell momentum 4-vector we can then use a boost into a frame where the fermion has on-shell momentum 4-vector $\pm p$,

$$\begin{pmatrix}\pm E\\ \mathbf{0}\end{pmatrix} \;\to\; \begin{pmatrix}\pm\sqrt{\boldsymbol{p}^2+m^2}\\ \pm\boldsymbol{p}\end{pmatrix} = \Lambda\cdot\begin{pmatrix}\pm m\\ \mathbf{0}\end{pmatrix}, \tag{H.23}$$

and equation (H.11) then implies

$$\psi(\pm\sqrt{\boldsymbol{p}^2+m^2},\pm\boldsymbol{p}) = U(\Lambda)\cdot\psi(\pm m,\mathbf{0}).$$

The Lorentz boost which takes us from the rest frame of the fermion into a frame where the fermion has on-shell momentum 4-vector $\pm p$ is

$$\begin{aligned}\Lambda(\boldsymbol{u}) = \{\Lambda^\mu{}_\nu(\boldsymbol{u})\} &= \begin{pmatrix}\gamma & -\gamma\boldsymbol{\beta}^T\\ -\gamma\boldsymbol{\beta} & \mathbf{1}-\hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T+\gamma\hat{\boldsymbol{u}}\otimes\hat{\boldsymbol{u}}^T\end{pmatrix}\\ &= \frac{1}{m}\begin{pmatrix}\sqrt{\boldsymbol{p}^2+m^2} & \boldsymbol{p}^T\\ \boldsymbol{p} & m\mathbf{1}-m\hat{\boldsymbol{p}}\otimes\hat{\boldsymbol{p}}^T+\sqrt{\boldsymbol{p}^2+m^2}\hat{\boldsymbol{p}}\otimes\hat{\boldsymbol{p}}^T\end{pmatrix},\end{aligned}$$

i.e. with $E(\boldsymbol{p}) \equiv \sqrt{\boldsymbol{p}^2 + m^2}$,

$$\gamma = \cosh(u) = \frac{1}{m}\sqrt{\boldsymbol{p}^2 + m^2} = \frac{E(\boldsymbol{p})}{m}, \quad \gamma\boldsymbol{\beta} = \hat{\boldsymbol{u}}\sinh(u) = -\frac{\boldsymbol{p}}{m}, \tag{H.24}$$

$$\boldsymbol{v} = \boldsymbol{\beta} = -\frac{\boldsymbol{p}}{\sqrt{\boldsymbol{p}^2 + m^2}}.$$

The minus sign makes perfect sense: We have to transform from the particle's rest frame into a frame which moves with speed $\boldsymbol{v} = -\boldsymbol{v}_{particle}$ relative to the particle to observe the particle with speed $\boldsymbol{v}_{particle} = \boldsymbol{p}/E(\boldsymbol{p})$.
The rapidity parameter is

$$u = \operatorname{artanh}(\beta) = \frac{1}{2}\ln\left(\frac{1+\beta}{1-\beta}\right) = \frac{1}{2}\ln\left(\frac{\sqrt{\boldsymbol{p}^2 + m^2} + |\boldsymbol{p}|}{\sqrt{\boldsymbol{p}^2 + m^2} - |\boldsymbol{p}|}\right)$$
$$= \ln\left(\frac{\sqrt{\boldsymbol{p}^2 + m^2} + |\boldsymbol{p}|}{m}\right).$$

The general boost matrix acting on the spinors is

$$U(\boldsymbol{u}) = \exp\bigl(\mathrm{i}u^i S_{i0}\bigr) = \exp\left(\frac{1}{2}u^i\gamma_0\gamma_i\right) = \cosh\left(\frac{u}{2}\right) + \hat{\boldsymbol{u}}\cdot\gamma_0\boldsymbol{\gamma}\sinh\left(\frac{u}{2}\right),$$

$$U^2(\boldsymbol{u}) = \exp\bigl(2\mathrm{i}u^i S_{i0}\bigr) = \exp\bigl(u^i\gamma_0\gamma_i\bigr) = \cosh(u) + \hat{\boldsymbol{u}}\cdot\gamma_0\boldsymbol{\gamma}\sinh(u).$$

In the present case we have

$$U^2(\boldsymbol{u}) = \frac{1}{m}\left(\sqrt{\boldsymbol{p}^2 + m^2} - \boldsymbol{p}\cdot\gamma_0\boldsymbol{\gamma}\right),$$

i.e. we can also write

$$U(\boldsymbol{u}) = \frac{1}{\sqrt{m}}\sqrt{\sqrt{\boldsymbol{p}^2 + m^2} - \boldsymbol{p}\cdot\gamma_0\boldsymbol{\gamma}}. \tag{H.25}$$

The corresponding boost matrices in the Dirac representation (21.29) are

$$\gamma_0\gamma_i = \begin{pmatrix} 0 & -\sigma_i \\ -\sigma_i & 0 \end{pmatrix},$$

$$U(\boldsymbol{u}) = \begin{pmatrix} \cosh\left(\frac{u}{2}\right) & -\hat{\boldsymbol{u}}^T\cdot\boldsymbol{\sigma}\sinh\left(\frac{u}{2}\right) \\ -\hat{\boldsymbol{u}}\cdot\boldsymbol{\sigma}\sinh\left(\frac{u}{2}\right) & \cosh\left(\frac{u}{2}\right) \end{pmatrix} = \frac{1}{\sqrt{m}}\begin{pmatrix} E(\boldsymbol{p}) & \boldsymbol{p}\cdot\boldsymbol{\sigma} \\ \boldsymbol{p}\cdot\boldsymbol{\sigma} & E(\boldsymbol{p}) \end{pmatrix}^{1/2}.$$

For the evaluation of the hyperbolic functions, we note

$$\cosh\left(\frac{u}{2}\right) = \sqrt{\frac{\cosh(u)+1}{2}} = \sqrt{\frac{E(\boldsymbol{p})+m}{2m}},$$
$$\sinh\left(\frac{u}{2}\right) = \sqrt{\frac{\cosh(u)-1}{2}} = \sqrt{\frac{E(\boldsymbol{p})-m}{2m}} = \frac{|\boldsymbol{p}|}{\sqrt{2m(E(\boldsymbol{p})+m)}}.$$

This yields

$$U(\boldsymbol{u}) = \frac{1}{\sqrt{2m(E(\boldsymbol{p})+m)}} \begin{pmatrix} E(\boldsymbol{p})+m & \boldsymbol{p}\cdot\boldsymbol{\sigma} \\ \boldsymbol{p}\cdot\boldsymbol{\sigma} & E(\boldsymbol{p})+m \end{pmatrix}. \tag{H.26}$$

The rest frame spinors satisfying equation (H.22) in the Dirac representation are

$$u(\mathbf{0}, \tfrac{1}{2}) = \begin{pmatrix} \sqrt{2m} \\ 0 \\ 0 \\ 0 \end{pmatrix}, \quad u(\mathbf{0}, -\tfrac{1}{2}) = \begin{pmatrix} 0 \\ \sqrt{2m} \\ 0 \\ 0 \end{pmatrix},$$

$$v(\mathbf{0}, -\tfrac{1}{2}) = \begin{pmatrix} 0 \\ 0 \\ \sqrt{2m} \\ 0 \end{pmatrix}, \quad v(\mathbf{0}, \tfrac{1}{2}) = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \sqrt{2m} \end{pmatrix},$$

and application of the spinor boost matrix (H.26) yields the spinors $u(\boldsymbol{p}, \pm\frac{1}{2})$ and $v(\boldsymbol{p}, \pm\frac{1}{2})$ in agreement with equations (21.35-21.38). The initial construction there from $m - \gamma \cdot p$ gave us the negative energy solutions $v(-\boldsymbol{p}, \pm\frac{1}{2})$ for momentum 4-vector $(-E(\boldsymbol{p}), \boldsymbol{p})$, whereas the construction from equation (H.23) gave us directly the negative energy solutions $v(\boldsymbol{p}, \pm\frac{1}{2})$ for momentum 4-vector $-p = (-E(\boldsymbol{p}), -\boldsymbol{p})$, which in either derivation are finally used in the general free solution (21.39).

Appendix I: Green's functions in d dimensions

We will not use summation convention in this appendix.
Green's functions are solutions of linear differential equations with δ function source terms. Basic one-dimensional examples are provided by the conditions

$$\frac{d}{dx}S(x) - \kappa S(x) = -\delta(x), \quad \frac{d^2}{dx^2}G(x) - \kappa^2 G(x) = -\delta(x), \tag{I.1}$$

with solutions

$$G(x) = \frac{a}{2\kappa}\exp(-\kappa|x|) + \frac{a-1}{2\kappa}\exp(\kappa|x|) + A\exp(\kappa x) + B\exp(-\kappa x), \tag{I.2}$$

and

$$\begin{aligned} S(x) &= \frac{d}{dx}G(x) + \kappa G(x) \\ &= a\Theta(-x)\exp(\kappa x) + (a-1)\Theta(x)\exp(\kappa x) + 2\kappa A\exp(\kappa x) \\ &= C\exp(\kappa x) + \Theta(-x)\exp(\kappa x) = C'\exp(\kappa x) - \Theta(x)\exp(\kappa x), \end{aligned} \tag{I.3}$$

$$C' = C + 1 = 2\kappa A + a.$$

That the functions (I.2,I.3) satisfy the conditions (I.1) is easily confirmed by using

$$\frac{d}{dx}|x| = \Theta(x) - \Theta(-x), \quad \frac{d}{dx}\Theta(\pm x) = \pm\delta(x).$$

The solutions of the conditions in the limit $\kappa \to 0$ are

$$G(x) = \alpha x + \beta - \frac{|x|}{2}, \quad S(x) = \frac{d}{dx}G(x) = \alpha + \frac{\Theta(-x) - \Theta(x)}{2}. \tag{I.4}$$

The appearance of integration constants signals that we can impose boundary conditions on the Green's functions. An important example for this is the requirement of vanishing Green's functions at spatial infinity, which can be imposed if the real part of κ does not vanish. For positive real κ this implies the one-dimensional Green's functions

$$G(x) = \frac{1}{2\kappa}\exp(-\kappa|x|), \quad S(x) = \Theta(-x)\exp(\kappa x).$$

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However, in one dimension we cannot satisfy the boundary condition of vanishing Green's functions at infinity if $\kappa = 0$, and we will find the same result for the scalar Green's function $G(\boldsymbol{x})$ in two dimensions. We can satisfy conditions that the Green's functions (I.4) should vanish on a half-axis $x < 0$ or $x > 0$ for $\kappa = 0$ by choosing $\alpha = \mp 1/2$, $\beta = 0$. On the other hand, if $\kappa = \mathrm{i}k$ is imaginary with $k > 0$, the Green's function

$$G(x) = \frac{\mathrm{i}}{2k} \exp(\mathrm{i}k|x|)$$

describes the spatial factor of outgoing waves $\exp[\mathrm{i}(k|x| - \omega t)]$, i.e the one-dimensional version of outgoing spherical waves.

Green's functions for Schrödinger's equation

We are mostly concerned with Green's functions associated with time-independent Hamilton operators

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}) = \int d^d\boldsymbol{x}\, |\boldsymbol{x}\rangle \left(-\frac{\hbar^2}{2m}\Delta + V(\boldsymbol{x}) \right) \langle \boldsymbol{x}|.$$

Note that the number of spatial dimensions d is left as a discrete variable. The inversion condition for the energy-dependent Schrödinger operator,

$$(E - H)\, \mathcal{G}_{d,V}(E) = 1 \tag{I.5}$$

is in $\boldsymbol{x}$ representation the condition

$$\left(E + \frac{\hbar^2}{2m}\Delta - V(\boldsymbol{x}) \right) \langle \boldsymbol{x}|\mathcal{G}_{d,V}(E)|\boldsymbol{x}'\rangle = \delta(\boldsymbol{x} - \boldsymbol{x}'). \tag{I.6}$$

The equations (I.5) and (I.6) show that we should rather talk about a Green's *operator* $\mathcal{G}_{d,V}(E)$ (or a *resolvent* in mathematical terms), with matrix elements $\langle \boldsymbol{x}|\mathcal{G}_{d,V}(E)|\boldsymbol{x}'\rangle$. We will instead continue to use the designation Green's function both for $\mathcal{G}_{d,V}(E)$ and the Fourier transformed operator $\mathcal{G}_{d,V}(t)$ and for all their representations in $\boldsymbol{x}$ or $\boldsymbol{k}$ space variables (or their matrix elements with respect to any other quantum states). The designation Green's function originated from the matrix elements $\mathcal{G}_{d,V}(\boldsymbol{x}, \boldsymbol{x}'; E) \equiv \langle \boldsymbol{x}|\mathcal{G}_{d,V}(E)|\boldsymbol{x}'\rangle$. These functions preceded the resolvent $\mathcal{G}_{d,V}(E)$ because the inception of differential equations preceded the discovery of abstract operator concepts and bra-ket notation.

The Green's function $\mathcal{G}_{d,V}(E)$ can eventually be calculated perturbatively in terms of the free Green's function $\mathcal{G}_d(E) \equiv \mathcal{G}_{d,V=0}(E)$. The equations

$$(E - H_0)\, \mathcal{G}_{d,V}(E) = 1 + V\mathcal{G}_{d,V}(E), \quad (E - H_0)\, \mathcal{G}_d(E) = 1,$$

yield

$$\begin{aligned} \mathcal{G}_{d,V}(E) &= \mathcal{G}_d(E) + \mathcal{G}_d(E)V\mathcal{G}_{d,V}(E) \\ &= \mathcal{G}_d(E) + \mathcal{G}_d(E)V\mathcal{G}_d(E) + \mathcal{G}_d(E)V\mathcal{G}_d(E)V\mathcal{G}_{d,V}(E) \\ &= \sum_{n=0}^{\infty} \mathcal{G}_d(E)\, (V\mathcal{G}_d(E))^n = \sum_{n=0}^{\infty} (\mathcal{G}_d(E)V)^n\, \mathcal{G}_d(E). \end{aligned} \tag{I.7}$$

Whether this formal iteration yields a sensible numerical approximation depends on the potential V, the energy E, and on the states for which we wish to calculate the corresponding matrix element of $\mathcal{G}_{d,V}(E)$. We defined $H_0 = \mathbf{p}^2/2m$ as the free Hamiltonian, and we have used the first two terms of (I.7) in potential scattering theory in the Born approximation. Other applications of series like (I.7) in perturbation theory would include a solvable part V_0 of the potential in H_0 and use only a perturbation $V' = V - V_0$ for the iterative solution. However, our main concern in the following will be the free Green's function $\mathcal{G}_d(E)$.

The variable E in (I.5) can be complex, but $\mathcal{G}_{d,V}(E)$ will become singular for values of E in the spectrum of H. It is therefore useful to explicitly add a small imaginary part if E is constrained to be real, which is the most relevant case for us. To discuss the implications of a small imaginary addition to E, consider Fourier transformation of (I.5) into the time domain. Substitution of

$$\mathcal{G}_{d,V}(E) = \int_{-\infty}^{\infty} dt\, \mathcal{G}_{d,V}(t) \exp(\mathrm{i}Et/\hbar), \tag{I.8}$$

$$\mathcal{G}_{d,V}(t) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dE\, \mathcal{G}_{d,V}(E) \exp(-\mathrm{i}Et/\hbar), \tag{I.9}$$

yields

$$\left(\mathrm{i}\hbar\frac{d}{dt} - H\right) \mathcal{G}_{d,V}(t) = \delta(t). \tag{I.10}$$

We can solve this equation in the form

$$\mathcal{G}_{d,V}(t) = \frac{a}{\mathrm{i}\hbar}\Theta(t)\mathcal{K}_{d,V}(t) + \frac{a-1}{\mathrm{i}\hbar}\Theta(-t)\mathcal{K}_{d,V}(t) = \frac{a - \Theta(-t)}{\mathrm{i}\hbar}\mathcal{K}_{d,V}(t), \tag{I.11}$$

if $\mathcal{K}_{d,V}(t)$ is the solution of the time-dependent Schrödinger equation

$$\left(\mathrm{i}\hbar\frac{d}{dt} - H\right) \mathcal{K}_{d,V}(t) = 0$$

with initial condition $\mathcal{K}_{d,V}(0) = 1$. Indeed, we have found this solution and used it extensively in Chapter 13. It is the time evolution operator

$$\mathcal{K}_{d,V}(t) = U(t) = \exp\left(-\frac{\mathrm{i}}{\hbar}Ht\right). \tag{I.12}$$

Equations (I.11) and (I.12) imply that the Green's function in the energy representation is

$$\begin{aligned}\mathcal{G}_{d,V}(E) &= \frac{a}{\mathrm{i}\hbar}\int_0^{\infty} dt\, \exp[\mathrm{i}(E - H + \mathrm{i}\epsilon)t/\hbar] \\ &\quad -\frac{1-a}{\mathrm{i}\hbar}\int_{-\infty}^{0} dt\, \exp[\mathrm{i}(E - H - \mathrm{i}\epsilon)t/\hbar] \\ &= \frac{a}{E - H + \mathrm{i}\epsilon} + \frac{1-a}{E - H - \mathrm{i}\epsilon},\end{aligned} \tag{I.13}$$

with a small shift $\epsilon > 0$.
The time-dependent Green's function (I.11) solves the inhomogeneous equation

$$\left(\mathrm{i}\hbar\frac{d}{dt} - H\right) F(t) = J(t)$$

in the form

$$\begin{aligned} F(t) &= F_0(t) + \int_{-\infty}^{\infty} dt'\, \mathcal{G}_{d,V}(t-t')J(t') \\ &= F_0(t) + \frac{a}{\mathrm{i}\hbar}\int_{-\infty}^{t} dt'\, \exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right) J(t') \\ &\quad + \frac{a-1}{\mathrm{i}\hbar}\int_{t}^{\infty} dt'\, \exp\left(-\frac{\mathrm{i}}{\hbar}H(t-t')\right) J(t'), \end{aligned} \tag{I.14}$$

where $F_0(t)$ is an arbitrary solution of the Schrödinger equation

$$\left(\mathrm{i}\hbar\frac{d}{dt} - H\right) F_0(t) = 0.$$

The Green's function (I.11,I.13) with $a = 1$ is the *retarded Green's function*, because the solution (I.14) receives only contributions from $J(t')$ at times $t' < t$ for $a = 1$. The Green's function with $a = 0$ is denoted as an *advanced Green's function*, because it determines $F(t)$ from back evolution of future values of $J(t)$.
We will now specialize to the retarded free Green's function. So far we have found the following representations for this Green's function,

$$\mathcal{G}_d(t) = \frac{\Theta(t)}{\mathrm{i}\hbar}\exp\left(-\frac{\mathrm{i}t}{2m\hbar}\mathbf{p}^2\right), \tag{I.15}$$

$$\mathcal{G}_d(E) = -\frac{2m}{\hbar^2}G_d(E) = \frac{1}{E + \mathrm{i}\epsilon - (\mathbf{p}^2/2m)}. \tag{I.16}$$

The rescaled Green's function $G_d(E)$ is an inverse Poincaré operator

$$\left(\Delta + \frac{2mE}{\hbar^2}\right)\langle \boldsymbol{x}|G_d(E)|\boldsymbol{x}'\rangle = -\delta(\boldsymbol{x} - \boldsymbol{x}'), \tag{I.17}$$

and has been introduced to make the connection with electromagnetic Green's functions and potentials more visible.
The equations (I.15,I.16) do not generate any spectacular dependence on the number d of spatial dimensions in the $\boldsymbol{k}$-space representation of the retarded free Green's functions,

$$\begin{aligned} \langle \boldsymbol{k}|\mathcal{G}_d(t)|\boldsymbol{k}'\rangle &= \frac{\Theta(t)}{\mathrm{i}\hbar}\exp\left(-\mathrm{i}\frac{\hbar t}{2m}\boldsymbol{k}^2\right)\delta(\boldsymbol{k} - \boldsymbol{k}') \equiv \mathcal{G}_d(\boldsymbol{k}, t)\delta(\boldsymbol{k} - \boldsymbol{k}'), \\ \langle \boldsymbol{k}|G_d(E)|\boldsymbol{k}'\rangle &= \frac{\delta(\boldsymbol{k} - \boldsymbol{k}')}{\boldsymbol{k}^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon} \equiv G_d(\boldsymbol{k}, E)\delta(\boldsymbol{k} - \boldsymbol{k}'), \end{aligned} \tag{I.18}$$

and also the d-dependence of the mixed representations is not particularly noteworthy, e.g.

$$\langle \boldsymbol{x}|\mathcal{G}_d(t)|\boldsymbol{k}\rangle = \langle \boldsymbol{x}|\boldsymbol{k}\rangle \mathcal{G}_d(\boldsymbol{k},t) = \frac{\Theta(t)}{\mathrm{i}\hbar\sqrt{2\pi}^d} \exp\left(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x} - \mathrm{i}\frac{\hbar t}{2m}\boldsymbol{k}^2\right),$$

$$\langle \boldsymbol{x}|G_d(E)|\boldsymbol{k}\rangle = \langle \boldsymbol{x}|\boldsymbol{k}\rangle G_d(\boldsymbol{k},E) = \frac{1}{\sqrt{2\pi}^d} \frac{\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})}{\boldsymbol{k}^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon}.$$

The $\boldsymbol{x}$-representation of the time-dependent Green's function,

$$\langle \boldsymbol{x}|\mathcal{G}_d(t)|\boldsymbol{x}'\rangle = \frac{1}{(2\pi)^d}\int d^d\boldsymbol{k}\, \mathcal{G}_d(\boldsymbol{k},t)\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')] \equiv \mathcal{G}_d(\boldsymbol{x}-\boldsymbol{x}',t),$$

is

$$\begin{aligned}\mathcal{G}_d(\boldsymbol{x},t) &= \frac{\Theta(t)}{\mathrm{i}\hbar(2\pi)^d}\int d^d\boldsymbol{k}\, \exp\left[\mathrm{i}\left(\boldsymbol{k}\cdot\boldsymbol{x} - \frac{\hbar t}{2m}\boldsymbol{k}^2\right)\right] \\ &= \frac{\Theta(t)}{\mathrm{i}\hbar}\sqrt{\frac{m}{2\pi\mathrm{i}\hbar t}}^d \exp\left(\mathrm{i}\frac{m\boldsymbol{x}^2}{2\hbar t}\right). \end{aligned} \tag{I.19}$$

This equation holds in the sense that $\mathcal{G}_d(\boldsymbol{x}-\boldsymbol{x}',t-t')$ has to be integrated with an absolutely or square integrable function $J(\boldsymbol{x}',t')$ to yield a solution $F(\boldsymbol{x},t)$ (I.14) of an inhomogeneous Schrödinger equation.

The representation of the retarded free Green's function in the time-domain is interesting in its own right, but in terms of dependence on the number d of dimensions, the operator $\mathrm{i}\hbar\mathcal{G}_d(t)$ and its representations $\mathrm{i}\hbar\mathcal{G}_d(\boldsymbol{k},t)$ and $\mathrm{i}\hbar\mathcal{G}_d(\boldsymbol{x},t)$ are simply products of d copies of the corresponding one-dimensional Green's function $\mathrm{i}\hbar\mathcal{G}_1(t)$ and its representations. Free propagation in time separates completely in spatial dimensions[19].

The interesting dimensional aspects of the Green's function appear if we represent it in the energy domain and in $\boldsymbol{x}$-space,

$$\begin{aligned}\langle \boldsymbol{x}|G_d(E)|\boldsymbol{x}'\rangle &= \frac{1}{(2\pi)^d}\int d^d\boldsymbol{k}\, G_d(\boldsymbol{k},E)\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')] \\ &\equiv G_d(\boldsymbol{x}-\boldsymbol{x}',E). \end{aligned} \tag{I.20}$$

This requires a little extra preparation.

Polar coordinates in d dimensions

Evaluation of the d-dimensional Fourier transformation in (I.20) involves polar coordinates in d-dimensional $\boldsymbol{k}$ space. Furthermore, it is also instructive to derive the zero energy Green's function $G_d(0)$ directly in $\boldsymbol{x}$ space, which is

[19] This is a consequence of the separation of the free non-relativistic Hamiltonian $H_0 = \mathbf{p}^2/2m$. However, this property does not hold in relativistic quantum mechanics, and therefore the free Green's function in the relativistic case is not a product of one-dimensional Green's functions, see (I.37).

also conveniently done in polar coordinates. Therefore we use $\boldsymbol{x}$ space as a paradigm for the discussion of polar coordinates in d dimensions with the understanding that in $\boldsymbol{k}$ space, $r = \sqrt{\boldsymbol{x}^2}$ is replaced with $k = \sqrt{\boldsymbol{k}^2}$.
We define polar coordinates $r, \theta_1, \dots \theta_{d-1}$ in d dimensions through

$$\begin{aligned} x_1 &= r \sin\theta_1 \cdot \sin\theta_2 \cdot \ldots \cdot \sin\theta_{d-2} \cdot \sin\theta_{d-1}, \quad \varphi = \frac{\pi}{2} - \theta_{d-1} \\ x_2 &= r \sin\theta_1 \cdot \sin\theta_2 \cdot \ldots \cdot \sin\theta_{d-2} \cdot \cos\theta_{d-1}, \\ &\vdots \\ x_{d-1} &= r \sin\theta_1 \cdot \cos\theta_2, \\ x_d &= r \cos\theta_1. \end{aligned}$$

This yields corresponding tangent vectors along the radial coordinate lines, cf. (5.16),

$$\boldsymbol{a}_r = \frac{\partial \boldsymbol{x}}{\partial r} = \boldsymbol{e}_r,$$

and along the θ_i coordinate lines

$$\boldsymbol{a}_i = \frac{\partial \boldsymbol{x}}{\partial \theta_i} = r \sin\theta_1 \cdot \sin\theta_2 \cdot \ldots \sin\theta_{i-1} \boldsymbol{e}_i.$$

Here we defined the unit tangent vector along the θ_i coordinate line

$$\boldsymbol{e}_i = \frac{\boldsymbol{a}_i}{|\boldsymbol{a}_i|}.$$

This should not be confused with Cartesian basis vectors since we do not use any Cartesian basis vector in this section.
The induced metric is $g_{\mu\nu} = \boldsymbol{a}_\mu \cdot \boldsymbol{a}_\nu$, see Section 5.4. This yields in the present case

$$g_{\mu\nu}\Big|_{\mu\neq\nu} = 0, \quad g_{rr} = 1,$$

and

$$g_{ii} = r^2 \sin^2\theta_1 \cdot \sin^2\theta_2 \cdot \ldots \cdot \sin^2\theta_{i-1}, \quad 1 \le i \le d-1.$$

The Jacobian determinant (5.26) of the transformation from polar to Cartesian coordinates and the related volume measure (5.25) are then

$$\sqrt{g} = r^{d-1} \sin^{d-2}\theta_1 \cdot \sin^{d-3}\theta_2 \cdot \ldots \cdot \sin\theta_{d-2}$$

and

$$d^d\boldsymbol{x} = dr d\theta_1 \ldots d\theta_{d-1}\, r^{d-1} \sin^{d-2}\theta_1 \cdot \sin^{d-3}\theta_2 \cdot \ldots \cdot \sin\theta_{d-2}.$$

In particular, the hypersurface area of the $(d-1)$-dimensional unit sphere is

$$S_{d-1} = 2\pi \prod_{n=1}^{d-2} \int_0^\pi d\theta \, \sin^n \theta = \frac{2\sqrt{\pi}^d}{\Gamma(d/2)}. \tag{I.21}$$

The gradient operator $\boldsymbol{\nabla} = \sum_\mu \boldsymbol{a}^\mu \partial_\mu$ is

$$\boldsymbol{\nabla} = \boldsymbol{e}_r \frac{\partial}{\partial r} + \sum_{i=1}^{d-1} \frac{\boldsymbol{e}_i}{r \sin\theta_1 \cdot \sin\theta_2 \cdot \ldots \cdot \sin\theta_{i-1}} \frac{\partial}{\partial \theta_i}.$$

For the calculation of the Laplace operator, we need the derivatives (recall that we do not use summation convention in this appendix)

$$\boldsymbol{e}_j \cdot \frac{\partial \boldsymbol{e}_r}{\partial \theta_j} = \sin\theta_1 \cdot \sin\theta_2 \cdot \ldots \sin\theta_{j-1}$$

and

$$\boldsymbol{e}_j \cdot \frac{\partial \boldsymbol{e}_i}{\partial \theta_j} = \delta_{j,i+1} \cos\theta_i + \Theta(j > i+1) \cos\theta_i \cdot \sin\theta_{i+1} \cdot \ldots \cdot \sin\theta_{j-1}.$$

This yields

$$\begin{aligned} \Delta = {} & \frac{\partial^2}{\partial r^2} + \frac{d-1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \sum_{i=1}^{d-1} \frac{1}{\sin^2\theta_1 \cdot \sin^2\theta_2 \cdot \ldots \cdot \sin^2\theta_{i-1}} \frac{\partial^2}{\partial \theta_i^2} \\ & + \frac{1}{r^2} \sum_{i=1}^{d-2} \sum_{j=i+1}^{d-1} \frac{\cot\theta_i}{\sin^2\theta_1 \cdot \sin^2\theta_2 \cdot \ldots \cdot \sin^2\theta_{i-1}} \frac{\partial}{\partial \theta_i}. \end{aligned}$$

We only need the radial part of the Laplace operator for the direct calculation of the zero energy Green's function $G_d(\boldsymbol{x}, E=0) \equiv G_d(r)$. The condition

$$\Delta G_d(r) = \frac{1}{r^{d-1}} \frac{d}{dr} r^{d-1} \frac{d}{dr} G_d(r) = -\delta(\boldsymbol{x})$$

implies after integration over a spherical volume with radius r,

$$S_{d-1} r^{d-1} \frac{d}{dr} G_d(r) = \frac{2\sqrt{\pi}^d}{\Gamma(d/2)} r^{d-1} \frac{d}{dr} G_d(r) = -1.$$

This yields

$$G_d(r) = \begin{cases} (a-r)/2, & d=1, \\ -(2\pi)^{-1} \ln(r/a), & d=2, \\ \Gamma\left(\frac{d-2}{2}\right) \left(4\sqrt{\pi}^d r^{d-2}\right)^{-1}, & d \geq 3. \end{cases} \tag{I.22}$$

The integration constant determines for $d=1$ and $d=2$ at which distance a the Green's function vanishes. For $d \geq 3$ the vanishing integration constant $\propto a^{2-d}$ is imposed by the usual boundary condition $\lim_{r\to\infty} G_{d\geq 3}(r) = 0$.

The full energy-dependent Green's function in $\boldsymbol{x}$-representation $\langle \boldsymbol{x}|G_d(E)|\boldsymbol{x}'\rangle \equiv G_d(\boldsymbol{x}-\boldsymbol{x}', E) = G_d(|\boldsymbol{x}-\boldsymbol{x}'|, E)$ can be gotten from integration of the condition

$$\Delta G_d(\boldsymbol{x}, E) + \frac{2m}{\hbar^2} E G_d(\boldsymbol{x}, E) = -\delta(\boldsymbol{x}). \tag{I.23}$$

The result (I.22) motivates an *ansatz*

$$G_d(\boldsymbol{x}, E) = f_d(r, E) G_d(r). \tag{I.24}$$

This will solve (I.23) if the factor $f_d(r, E)$ satisfies

$$\frac{d^2}{dr^2} f_d(r, E) + \frac{3-d}{r} \frac{d}{dr} f_d(r, E) + \frac{2m}{\hbar^2} E f_d(r, E) = 0, \quad f_d(0, E) = 1.$$

This yields together with the requirement $G_d(\boldsymbol{x}, E)|_{E<0} \in \mathbb{R}$ and analyticity in E (and the convention $\sqrt{-E}|_{E>0} = -\mathrm{i}\sqrt{E}$),

$$\begin{aligned} G_d(\boldsymbol{x}, E) = {} & \frac{\Theta(-E)}{\sqrt{2\pi}^d} \left(\frac{\sqrt{-2mE}}{\hbar r}\right)^{\frac{d-2}{2}} K_{\frac{d-2}{2}}\left(\sqrt{-2mE}\frac{r}{\hbar}\right) \\ & + \mathrm{i}\frac{\pi}{2} \frac{\Theta(E)}{\sqrt{2\pi}^d} \left(\frac{\sqrt{2mE}}{\hbar r}\right)^{\frac{d-2}{2}} H^{(1)}_{\frac{d-2}{2}}\left(\sqrt{2mE}\frac{r}{\hbar}\right), \end{aligned} \tag{I.25}$$

where the conventions and definitions from [1] were used for the modified Bessel and Hankel functions.
The result (I.25) tells us that outgoing spherical waves of energy $E > 0$ in d dimensions are given by Hankel functions,

$$G_d(\boldsymbol{x}, E > 0) = \frac{\mathrm{i}\pi}{2\sqrt{2\pi}^d} \left(\frac{\sqrt{2mE}}{\hbar r}\right)^{\frac{d-2}{2}} H^{(1)}_{\frac{d-2}{2}}\left(\sqrt{2mE}\frac{r}{\hbar}\right),$$

while d-dimensional Yukawa potentials of range a are described by modified Bessel functions,

$$V_d(r) = \frac{1}{\sqrt{2\pi}^d r^{d-2}} \left(\frac{r}{a}\right)^{\frac{d-2}{2}} K_{\frac{d-2}{2}}\left(\frac{r}{a}\right),$$

with asymptotic form

$$V_d(r \gg a) \simeq \frac{\exp(-r/a)}{2\sqrt{a}^{d-3}\sqrt{2\pi r}^{d-1}}.$$

The result (I.25) can also be derived through Fourier transformation (I.20) from the energy-dependent retarded Green's function in $\boldsymbol{k}$ space,

$$\begin{aligned} G_d(\boldsymbol{x}, E) &= \frac{1}{(2\pi)^d} \int d^d\boldsymbol{k}\, G_d(\boldsymbol{k}, E) \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}), \\ G_d(\boldsymbol{k}, E) &= \frac{1}{\boldsymbol{k}^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon}, \end{aligned}$$

or in terms of poles in the complex k plane (where $k \equiv |\boldsymbol{k}|$ for $d > 1$),

$$G_d(\boldsymbol{k}, E) = \frac{\Theta(E)}{(k - \sqrt{2mE/\hbar^2} - \mathrm{i}\epsilon)(k + \sqrt{2mE/\hbar^2} + \mathrm{i}\epsilon)} + \frac{\Theta(-E)}{(k - \mathrm{i}\sqrt{-2mE/\hbar^2})(k + \mathrm{i}\sqrt{-2mE/\hbar^2})}. \tag{I.26}$$

This yields for $d > 1$ (for the ϑ integral see [30], p. 457, no. 6)

$$\begin{aligned} G_d(\boldsymbol{x}, E) &= \frac{S_{d-2}}{(2\pi)^d} \int_0^\infty dk \int_0^\pi d\vartheta \, \frac{k^{d-1} \exp(\mathrm{i}kr\cos\vartheta)}{k^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon} \sin^{d-2}\vartheta \\ &= \frac{1}{2^{d-1}\sqrt{\pi}^{d+1}\Gamma\left(\frac{d-1}{2}\right)} \int_0^\infty dk \int_0^\pi d\vartheta \, \frac{k^{d-1} \exp(\mathrm{i}kr\cos\vartheta)}{k^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon} \sin^{d-2}\vartheta \\ &= \frac{1}{\sqrt{2\pi}^d \sqrt{r}^{d-2}} \int_0^\infty dk \, \frac{\sqrt{k}^d}{k^2 - (2mE/\hbar^2) - \mathrm{i}\epsilon} J_{\frac{d-2}{2}}(kr) \\ &= \frac{\Theta(-E)}{\sqrt{2\pi}^d} \left(\frac{\sqrt{-2mE}}{\hbar r}\right)^{\frac{d-2}{2}} K_{\frac{d-2}{2}}\left(\sqrt{-2mE}\frac{r}{\hbar}\right) \\ &\quad + \mathrm{i}\frac{\pi}{2}\frac{\Theta(E)}{\sqrt{2\pi}^d} \left(\frac{\sqrt{2mE}}{\hbar r}\right)^{\frac{d-2}{2}} H^{(1)}_{\frac{d-2}{2}}\left(\sqrt{2mE}\frac{r}{\hbar}\right). \end{aligned} \tag{I.27}$$

For the k integral for $E > 0$ see [31], p. 179, no. 28. The real part of the integral for $E < 0$ is given on p. 179, no. 35. The integrals can also be performed with symbolic computation programs, of course. The k integral actually diverges for $d \geq 5$, but recall that we have found the same solution for arbitrary d from the *ansatz* (I.24). Fourier transformation of (I.26) for $d = 1$ directly yields the result (20.6), which also coincides with (I.27) for $d = 1$.

The time evolution operator in various representations

We have seen that the Green's function $\mathcal{G}_{d,V}(t)$ in the time domain is intimately connected to the time evolution operator

$$U(t) = \exp(-\mathrm{i}Ht/\hbar)$$

through equations (I.11,I.12). We can also define an energy representation for the time evolution operator in analogy to equations (I.8,I.9),

$$U(E) = \int_{-\infty}^{\infty} dt \, U(t) \exp(\mathrm{i}Et/\hbar) = 2\pi\hbar\delta(E - H). \tag{I.28}$$

The free d-dimensional evolution operator in the time domain is simply the product of d one-dimensional evolution operators,

$$U_0(t) = \exp\left(-\frac{\mathrm{i}t}{2m\hbar}\mathbf{p}^2\right),$$

$$\langle \boldsymbol{k}|U_0(t)|\boldsymbol{k}'\rangle = U_0(\boldsymbol{k},t)\delta(\boldsymbol{k}-\boldsymbol{k}'), \quad U_0(\boldsymbol{k},t) = \exp\left(-\mathrm{i}\frac{\hbar t}{2m}\boldsymbol{k}^2\right),$$

$$\langle \boldsymbol{x}|U_0(t)|\boldsymbol{k}\rangle = \frac{1}{\sqrt{2\pi}^d}\exp\left(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x} - \mathrm{i}\frac{\hbar t}{2m}\boldsymbol{k}^2\right),$$

and

$$\langle \boldsymbol{x}|U_0(t)|\boldsymbol{x}'\rangle = \frac{1}{(2\pi)^d}\int d^3\boldsymbol{k}\,\exp[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]\,U_0(\boldsymbol{k},t) = U_0(\boldsymbol{x}-\boldsymbol{x}',t),$$

$$U_0(\boldsymbol{x},t) = \sqrt{\frac{m}{2\pi\mathrm{i}\hbar t}}^d\,\exp\left(\mathrm{i}\frac{m\boldsymbol{x}^2}{2\hbar t}\right).$$

Just like for the free Green's functions, the dependence on d becomes more interesting in the energy domain. The equation

$$U_0(\boldsymbol{k},E) = 2\pi\hbar\delta\left(E - \frac{\hbar^2\boldsymbol{k}^2}{2m}\right) = \pi\sqrt{\frac{2m}{E}}\delta\left(|\boldsymbol{k}| - \frac{\sqrt{2mE}}{\hbar}\right)$$

yields

$$\begin{aligned} U_0(\boldsymbol{x},E) &= \frac{1}{(2\pi)^d}\int d^d\boldsymbol{k}\,\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})U_0(\boldsymbol{k},E) \\ &= \frac{\Theta(E)S_{d-2}}{2^d(\pi\hbar)^{d-1}}\sqrt{2m}^d\sqrt{E}^{d-2}\int_0^\pi d\vartheta\,\exp\left(\mathrm{i}\sqrt{2mE}\frac{r}{\hbar}\cos\vartheta\right)\sin^{d-2}\vartheta \\ &= \Theta(E)\frac{m}{\hbar}\left(\frac{1}{\pi\hbar r}\sqrt{\frac{mE}{2}}\right)^{\frac{d-2}{2}} J_{\frac{d-2}{2}}\left(\sqrt{2mE}\frac{r}{\hbar}\right). \end{aligned} \tag{I.29}$$

We have encountered several incarnations of the time evolution equation

$$|\psi(t)\rangle = U_0(t-t')|\psi(t')\rangle,$$

e.g. with $\langle \boldsymbol{k}|\psi\rangle \equiv \langle \boldsymbol{k}|\psi(0)\rangle$,

$$\begin{aligned} \langle \boldsymbol{x}|\psi(t)\rangle &= \int d^d\boldsymbol{k}\,\langle \boldsymbol{x}|U_0(t)|\boldsymbol{k}\rangle\langle \boldsymbol{k}|\psi\rangle \\ &= \frac{1}{\sqrt{2\pi}^d}\int d^d\boldsymbol{k}\,\exp\left[\mathrm{i}\left(\boldsymbol{k}\cdot\boldsymbol{x} - \frac{\hbar t}{2m}\boldsymbol{k}^2\right)\right]\psi(\boldsymbol{k}) \\ &= \int d^d\boldsymbol{x}'\,U_0(\boldsymbol{x}-\boldsymbol{x}',t-t')\langle \boldsymbol{x}'|\psi(t')\rangle. \end{aligned}$$

Equation (I.29) implies with $|\psi\rangle \equiv |\psi(t=0)\rangle$ the representation

$$\begin{aligned}\langle \boldsymbol{x}|\psi(E)\rangle &= \int dt\, \exp(\mathrm{i}Et/\hbar)\, \langle \boldsymbol{x}|\psi(t)\rangle \\ &= \int d^d\boldsymbol{x}' \int dt\, \exp(\mathrm{i}Et/\hbar)\, \langle \boldsymbol{x}|U_0(t)|\boldsymbol{x}'\rangle\langle \boldsymbol{x}'|\psi\rangle \\ &= \int d^d\boldsymbol{x}'\, \langle \boldsymbol{x}|U_0(E)|\boldsymbol{x}'\rangle\langle \boldsymbol{x}'|\psi\rangle \\ &= \Theta(E)\frac{m}{\hbar}\left(\frac{1}{\pi\hbar}\sqrt{\frac{mE}{2}}\right)^{\frac{d-2}{2}} \\ &\quad \times \int d^d\boldsymbol{x}'\, J_{\frac{d-2}{2}}\left(\sqrt{2mE}\frac{|\boldsymbol{x}-\boldsymbol{x}'|}{\hbar}\right)\frac{\langle \boldsymbol{x}'|\psi\rangle}{\sqrt{|\boldsymbol{x}-\boldsymbol{x}'|}^{d-2}}. \end{aligned} \tag{I.30}$$

However, recall that the states $|\psi(E)\rangle$ in the energy domain exist only in the distribution sense (5.12).

Relativistic Green's functions in d spatial dimensions

The relativistic free scalar Green's function in the time domain must satisfy

$$\left(\Delta - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\right) G_d(\boldsymbol{x},t;\boldsymbol{x}',t') = -\delta(\boldsymbol{x}-\boldsymbol{x}')\delta(t-t'). \tag{I.31}$$

This yields after transformation into $k = (\omega/c, \boldsymbol{k})$ space

$$G_d(\boldsymbol{k},\omega;\boldsymbol{k}',\omega') = G_d(\boldsymbol{k},\omega)\delta(\boldsymbol{k}-\boldsymbol{k}')\delta(\omega-\omega'),$$

where the factor $G_d(\boldsymbol{k},\omega)$ is

$$G_d(\boldsymbol{k},\omega) = \frac{1}{\boldsymbol{k}^2 - \frac{\omega^2}{c^2} + \frac{m^2c^2}{\hbar^2} - \mathrm{i}\epsilon}. \tag{I.32}$$

The shift $-\mathrm{i}\epsilon$, $\epsilon > 0$, into the complex plane is such that this reproduces the retarded non-relativistic Green's function (I.18) in the non-relativistic limit

$$\omega \Rightarrow \frac{mc^2 + E}{\hbar},$$

when terms of order $\mathcal{O}(E^2)$ are neglected. However, in the relativistic case this yields both retarded and advanced contributions in the time domain. This convention for the poles defines the relativistic Green's functions of Stückelberg and Feynman.
The solution in $x = (ct, \boldsymbol{x})$ space is then

$$G_d(\boldsymbol{x},t;\boldsymbol{x}',t') = G_d(\boldsymbol{x}-\boldsymbol{x}',t-t'),$$

$$G_d(\boldsymbol{x},t) = \frac{1}{2\pi}\int d\omega\, G_d(\boldsymbol{x},\omega)\exp(-\mathrm{i}\omega t), \tag{I.33}$$

$$G_d(\boldsymbol{x},\omega) = \frac{1}{(2\pi)^d}\int d^d\boldsymbol{k}\, G_d(\boldsymbol{k},\omega)\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}). \tag{I.34}$$

The integral is the same as in (I.27) with the substitution

$$\frac{2m}{\hbar^2}E \to \frac{\omega^2}{c^2} - \frac{m^2c^2}{\hbar^2},$$

i.e.

$$\begin{aligned} G_d(\boldsymbol{x},\omega) = {} & \frac{\Theta(mc^2-\hbar|\omega|)}{\sqrt{2\pi}^d}\left(\frac{\sqrt{m^2c^4-\hbar^2\omega^2}}{\hbar cr}\right)^{\frac{d-2}{2}} \\ & \times K_{\frac{d-2}{2}}\left(\sqrt{m^2c^4-\hbar^2\omega^2}\,\frac{r}{\hbar c}\right) \\ & +\mathrm{i}\frac{\pi}{2}\frac{\Theta(\hbar|\omega|-mc^2)}{\sqrt{2\pi}^d}\left(\frac{\sqrt{\hbar^2\omega^2-m^2c^4}}{\hbar cr}\right)^{\frac{d-2}{2}} \\ & \times H^{(1)}_{\frac{d-2}{2}}\left(\sqrt{\hbar^2\omega^2-m^2c^4}\,\frac{r}{\hbar c}\right). \end{aligned} \tag{I.35}$$

The $\omega = 0$ Green's functions

$$\left(\Delta - \frac{m^2c^2}{\hbar^2}\right)G_d(\boldsymbol{x}) = -\delta(\boldsymbol{x}), \quad G_d(\boldsymbol{x}) = \frac{1}{\sqrt{2\pi}^d}\left(\frac{mc}{\hbar r}\right)^{\frac{d-2}{2}} K_{\frac{d-2}{2}}\left(\frac{mc}{\hbar}r\right),$$

yield again the results (I.22) in the limit $m \to 0$, albeit with diverging integration constants in low dimensions,

$$a_{d=1} = \frac{\hbar}{mc}, \quad a_{d=2} = \frac{2\hbar}{mc}\exp(-\gamma).$$

In terms of poles in the complex k plane, the complex shift in (I.32) implies

$$\begin{aligned} G_d(\boldsymbol{k},\omega) = {} & \frac{c^2\Theta(\hbar\omega-mc^2)}{\left(ck-\sqrt{\omega^2-(mc^2/\hbar)^2}-\mathrm{i}\epsilon\right)\left(ck+\sqrt{\omega^2-(mc^2/\hbar)^2}+\mathrm{i}\epsilon\right)} \\ & +\frac{c^2\Theta(mc^2-\hbar\omega)}{\left(ck-\mathrm{i}\sqrt{(mc^2/\hbar)^2-\omega^2}\right)\left(ck-\mathrm{i}\sqrt{(mc^2/\hbar)^2-\omega^2}\right)}. \end{aligned} \tag{I.36}$$

However, in terms of poles in the complex ω plane, equation (I.32) implies

$$G_d(\boldsymbol{k},\omega) = -\frac{c^2}{\left(\omega-c\sqrt{k^2+(mc/\hbar)^2}+\mathrm{i}\epsilon\right)\left(\omega+c\sqrt{k^2+(mc/\hbar)^2}-\mathrm{i}\epsilon\right)}.$$

Fourier transformation to the time domain therefore yields a representation of the relativistic free Green's function which explicitly shows the combination of

retarded positive frequency and advanced negative frequency components,

$$\begin{aligned} G_d(\boldsymbol{k},t) &= \frac{1}{2\pi}\int d\omega\, G_d(\boldsymbol{k},\omega)\exp(-\mathrm{i}\omega t) \\ &= \mathrm{i}c\Theta(t)\frac{\exp\left(-\mathrm{i}\sqrt{\boldsymbol{k}^2+(mc/\hbar)^2}\,ct\right)}{2\sqrt{\boldsymbol{k}^2+(mc/\hbar)^2}} \\ &\quad +\mathrm{i}c\Theta(-t)\frac{\exp\left(\mathrm{i}\sqrt{\boldsymbol{k}^2+(mc/\hbar)^2}\,ct\right)}{2\sqrt{\boldsymbol{k}^2+(mc/\hbar)^2}}. \end{aligned} \tag{I.37}$$

On the other hand, shifting both poles into the lower complex ω plane,

$$G_d^{(r)}(\boldsymbol{k},\omega) = -\frac{c^2}{\left(\omega - c\sqrt{k^2+(mc/\hbar)^2}+\mathrm{i}\epsilon\right)\left(\omega + c\sqrt{k^2+(mc/\hbar)^2}+\mathrm{i}\epsilon\right)},$$

yields the retarded relativistic free Green's function

$$\begin{aligned} G_d^{(r)}(\boldsymbol{k},t) &= \frac{1}{2\pi}\int d\omega\, G_d^{(r)}(\boldsymbol{k},\omega)\exp(-\mathrm{i}\omega t) \\ &= c\Theta(t)\frac{\sin\left(\sqrt{\boldsymbol{k}^2+(mc/\hbar)^2}\,ct\right)}{\sqrt{\boldsymbol{k}^2+(mc/\hbar)^2}} = c^2\Theta(t)\mathcal{K}_d(\boldsymbol{k},t), \end{aligned} \tag{I.38}$$

cf. equation (21.6). If $\mathcal{K}_d(\boldsymbol{x},t)$ exists, then one can easily verify that the properties

$$\left(\Delta - \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{m^2c^2}{\hbar^2}\right)\mathcal{K}_d(\boldsymbol{x},t) = 0,$$

$$\mathcal{K}_d(\boldsymbol{x},0) = 0, \quad \frac{\partial}{\partial t}\mathcal{K}_d(\boldsymbol{x},t)\bigg|_{t=0} = \delta(\boldsymbol{x})$$

imply that $G_d^{(r)}(\boldsymbol{x},t) = c^2\Theta(t)\mathcal{K}_d(\boldsymbol{x},t)$ is a retarded Green's function.

Retarded relativistic Green's functions in $(\boldsymbol{x},t)$ representation

Evaluation of the Green's functions $G_d^{(r)}(\boldsymbol{x},t)$ and $G_d(\boldsymbol{x},t)$ for the massive Klein-Gordon equation is very cumbersome if one uses standard Fourier transformation between time and frequency. It is much more convenient to use Fourier transformation with imaginary frequency, which is known as Laplace transformation. We will demonstrate this for the retarded Green's function. The Laplace transform of $G_d^{(r)}(\boldsymbol{x},t)$ is

$$g_d(\boldsymbol{x},w) = \int_0^\infty dt\, \exp(-wt)G_d^{(r)}(\boldsymbol{x},t). \tag{I.39}$$

The completeness relation for Fourier monomials,

$$\delta(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \exp(-\mathrm{i}\omega t) = \frac{1}{2\pi\mathrm{i}}\int_{-\mathrm{i}\infty}^{\mathrm{i}\infty} dw\, \exp(wt)$$

then yields the inversion of (I.39),

$$G_d^{(r)}(\boldsymbol{x},t) = \frac{1}{2\pi\mathrm{i}}\int_{-\mathrm{i}\infty}^{\mathrm{i}\infty} dw\, \exp(wt) g_d(\boldsymbol{x},w). \tag{I.40}$$

The condition (I.31) on the d-dimensional scalar Green's functions then implies

$$\left(\Delta - \frac{w^2}{c^2} - \frac{m^2c^2}{\hbar^2}\right) g_d(\boldsymbol{x},w) = -\delta(\boldsymbol{x}) \tag{I.41}$$

with solution

$$g_d(\boldsymbol{x},w) = \frac{1}{(2\pi)^d}\int d^d\boldsymbol{k}\, \frac{\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x})}{\boldsymbol{k}^2 + (w/c)^2 + (mc/\hbar)^2}.$$

In one dimension this yields

$$g_1(x,w) = \frac{c\exp\left(-\sqrt{w^2+(mc^2/\hbar)^2}\,|x|/c\right)}{2\sqrt{w^2+(mc^2/\hbar)^2}}. \tag{I.42}$$

In higher dimensions, we need to calculate

$$\begin{aligned} g_d(\boldsymbol{x},w) &= \frac{S_{d-2}}{(2\pi)^d}\int_0^\infty dk \int_0^\pi d\vartheta\, k^{d-1}\sin^{d-2}\vartheta\, \frac{\exp(\mathrm{i}kr\cos\vartheta)}{k^2+(w/c)^2+(mc/\hbar)^2} \\ &= \frac{1}{\sqrt{2\pi}^d}\int_0^\infty dk\, \frac{k^{d-1}}{k^2+(w/c)^2+(mc/\hbar)^2}\frac{1}{\sqrt{kr}^{d-2}} J_{\frac{d-2}{2}}(kr). \end{aligned} \tag{I.43}$$

We can formally reduce (I.43) for $d \geq 3$ to the corresponding integrals in lower dimensions by using the relation

$$\left(-\frac{1}{x}\frac{d}{dx}\right)^n \frac{J_\nu(x)}{x^\nu} = \frac{J_{\nu+n}(x)}{x^{\nu+n}},$$

see number 9.1.30, p. 361 in [1]. This yields for $d = 2n+1$

$$\begin{aligned} \frac{1}{\sqrt{kr}^{d-2}} J_{\frac{d-2}{2}}(kr) &= k^{-2n}\left(-\frac{1}{r}\frac{\partial}{\partial r}\right)^n \sqrt{kr} J_{-\frac{1}{2}}(kr) \\ &= \sqrt{\frac{2}{\pi}} k^{-2n}\left(-\frac{1}{r}\frac{\partial}{\partial r}\right)^n \cos(kr), \end{aligned} \tag{I.44}$$

and for $d = 2n+2$,

$$\frac{1}{\sqrt{kr}^{d-2}} J_{\frac{d-2}{2}}(kr) = k^{-2n}\left(-\frac{1}{r}\frac{\partial}{\partial r}\right)^n J_0(kr). \tag{I.45}$$

The resulting relations for the Green's functions in the $(\boldsymbol{x}, w)$ representations are then

$$g_{2n+1}(\boldsymbol{x}, w) = \left(-\frac{1}{2\pi r}\frac{\partial}{\partial r}\right)^n \frac{1}{\pi}\int_0^\infty dk\, \frac{\cos(kr)}{k^2 + (w/c)^2 + (mc/\hbar)^2}$$
$$= \left(-\frac{1}{2\pi r}\frac{\partial}{\partial r}\right)^n \frac{c\exp\left(-\sqrt{w^2 + (mc^2/\hbar)^2}\, r/c\right)}{2\sqrt{w^2 + (mc^2/\hbar)^2}}, \tag{I.46}$$

and

$$g_{2n+2}(\boldsymbol{x}, w) = \left(-\frac{1}{2\pi r}\frac{\partial}{\partial r}\right)^n \frac{1}{\pi}\int_0^\infty dk\, \frac{kJ_0(kr)}{k^2 + (w/c)^2 + (mc/\hbar)^2}$$
$$= \left(-\frac{1}{2\pi r}\frac{\partial}{\partial r}\right)^n \frac{1}{2\pi} K_0\left(\sqrt{w^2 + (mc^2/\hbar)^2}\frac{r}{c}\right). \tag{I.47}$$

Inverse Laplace transformation yields the retarded Green's functions $G_d^{(r)}(\boldsymbol{x}, t)$,

$$G_{2n+1}^{(r)}(\boldsymbol{x}, t) = \left(-\frac{1}{2\pi r}\frac{\partial}{\partial r}\right)^n \frac{c}{2}\Theta(ct - r)J_0\left(mc\sqrt{c^2t^2 - r^2}/\hbar\right), \tag{I.48}$$

$$G_{2n+2}^{(r)}(\boldsymbol{x}, t) = \left(-\frac{1}{2\pi r}\frac{\partial}{\partial r}\right)^n \frac{c}{2\pi}\frac{\Theta(ct - r)}{\sqrt{c^2t^2 - r^2}}\cos\left(mc\sqrt{c^2t^2 - r^2}/\hbar\right). \tag{I.49}$$

The retarded relativistic Green's functions in one, two and three dimensions are therefore

$$G_1^{(r)}(x, t) = \frac{c}{2}\Theta(ct - |x|)J_0\left(mc\sqrt{c^2t^2 - x^2}/\hbar\right),$$

$$G_2^{(r)}(\boldsymbol{x}, t) = \frac{c}{2\pi}\frac{\Theta(ct - r)}{\sqrt{c^2t^2 - r^2}}\cos\left(mc\sqrt{c^2t^2 - r^2}/\hbar\right),$$

and

$$G_3^{(r)}(\boldsymbol{x}, t) = \frac{c}{4\pi r}\delta(r - ct) - \frac{mc^2}{4\pi\hbar}\frac{\Theta(ct - r)}{\sqrt{c^2t^2 - r^2}}J_1\left(mc\sqrt{c^2t^2 - r^2}/\hbar\right). \tag{I.50}$$

The functions $G_{d\geq 4}^{(r)}(\boldsymbol{x}, t)$ and $\mathcal{K}_{d\geq 4}(\boldsymbol{x}, t)$ do not exist, but the corresponding functions $G_d^{(r)}(\boldsymbol{k}, t) = c^2\Theta(t)\mathcal{K}_d(\boldsymbol{k}, t)$ (I.38) and $G_d^{(r)}(\boldsymbol{k}, \omega)$ exist in any nunmber of dimensions.

Liénard-Wiechert potentials in low dimensions

The massless retarded Green's functions solve the basic electromagnetic wave equation for the electromagnetic potentials in Lorentz gauge,

$$\left(\partial_\mu\partial^\mu - \frac{m^2c^2}{\hbar^2}\right)A^\nu(x) = -\mu_0 j^\nu(x), \quad \partial_\mu A^\mu(x) = 0,$$

$$A^\mu(x) = \mu_0\int d^{d+1}x'\,\frac{1}{c}G_d^{(r)}(x - x')j^\mu(x').$$

In three dimensions this yields the familiar Liénard-Wiechert potentials from the contributions of the currents on the backward light cone of the space-time point x,

$$A^\mu_{d=3}(\boldsymbol{x},t) = \frac{\mu_0}{4\pi}\int d^3\boldsymbol{x}'\,\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\,j^\mu\left(\boldsymbol{x}',t-\frac{1}{c}|\boldsymbol{x}-\boldsymbol{x}'|\right).$$

However, in one and two dimensions, the Liénard-Wiechert potentials sample charges and currents from the complete region inside the backward light cone,

$$A^\mu_{d=1}(x,t) = \frac{\mu_0 c}{2}\int_{-\infty}^{\infty}dx'\int_{-\infty}^{t-(|x-x'|/c)}dt'\,j^\mu(x',t'),$$

$$A^\mu_{d=2}(\boldsymbol{x},t) = \frac{\mu_0 c}{2\pi}\int d^2\boldsymbol{x}'\int_{-\infty}^{t-(|\boldsymbol{x}-\boldsymbol{x}'|/c)}dt'\,\frac{j^\mu(\boldsymbol{x}',t')}{\sqrt{c^2(t-t')^2-(\boldsymbol{x}-\boldsymbol{x}')^2}}.$$

Stated differently, a δ function type charge-current fluctuation in the space-time point x' generates an outwards traveling spherical electromagnetic perturbation on the forward light cone starting in x' if we are in three spatial dimensions. However, in one dimension the same kind of perturbation fills the whole forward light cone uniformly with electromagnetic fields, and in two dimensions the forward light cone is filled with a weight factor $[c^2(t-t')^2-(\boldsymbol{x}-\boldsymbol{x}')^2]^{-1/2}$. How can that be? The electrostatic potentials (I.22) for $d=1$ and $d=2$ hold the answer to this. Those potentials indicate linear or logarithmic confinement of electric charges in low dimensions. Therefore a positive charge fluctuation in a point x' must be compensated by a corresponding negative charge fluctuation nearby. Both fluctuations fill their overlapping forward light cones with opposite electromagnetic fields, but those fields will exactly compensate in the overlapping parts in one dimension, and largely compensate in two dimensions. The net effect of these opposite charge fluctuations at a distance a is then electromagnetic fields along a forward light cone of thickness a, i.e. electromagnetic confinement in low dimensions effectively ensures again that electromagnetic fields propagate along light cones. This is illustrated in Figure I.1.

Green's functions for Dirac operators in d dimensions

The Green's functions for the free Dirac operator must satisfy.

$$\left(\mathrm{i}\gamma^\mu\partial_\mu-\frac{mc}{\hbar}\right)S_d(\boldsymbol{x},t) = -\delta(\boldsymbol{x})\delta(t). \tag{I.51}$$

Since the Dirac operator is a factor of the Klein-Gordon operator, the solutions of the equations (I.51) and (I.31) are related by

$$S_d(\boldsymbol{x},t) = \left(\mathrm{i}\gamma^\mu\partial_\mu+\frac{mc}{\hbar}\right)G_d(\boldsymbol{x},t) \tag{I.52}$$

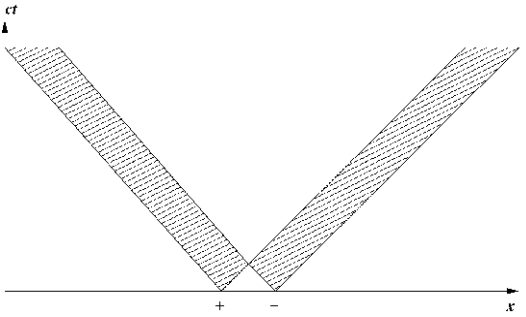


Figure I.1: The contributions of nearby opposite charge fluctuations at time $t = 0$ in one spatial dimension generate net electromagnetic fields in the hatched "thick" light cone region.

and

$$G_d(\boldsymbol{x},t) = \int d^d\boldsymbol{x}' \int dt'\, S_d(\boldsymbol{x}'-\boldsymbol{x},t'-t)\cdot S_d(\boldsymbol{x}',t') = \int d^d\boldsymbol{x}' \int dt'\, S_d(\boldsymbol{x}',t')\cdot S_d(\boldsymbol{x}'+\boldsymbol{x},t'+t). \tag{I.53}$$

The free Dirac Green's function in wave number representation is (here $k^2 \equiv k^\mu k_\mu$)

$$S_d(k) = \hbar\frac{mc-\hbar\gamma^\mu k_\mu}{\hbar^2k^2+m^2c^2-\mathrm{i}\epsilon}, \tag{I.54}$$

where the pole shifts again correspond to the Stückelberg-Feynman propagator with retarded and advanced components.

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Index

δ function, 25
ϵ tensor, 112
γ matrices, 424, 507
  Construction in d dimensions, 509
  Dirac basis, 424
  Invariance under Lorentz transformations, 519
  Weyl basis, 424
f-sum rule, 268
2-spinor, 141

Absorption cross section, 231
Active transformation, 72
Adjoint operator, 69
Amplitude vector, 376
Angular momentum, 111
  in relative motion, 107
Angular momentum operator, 111
  in polar coordinates, 111
Annihilation operator, 93
  for non-relativistic particles, 289
  for photons, 328
  for relativistic fermions, 428
  for relativistic scalar particles, 416
Anti-commutator, 284
Auger process, 228

Baker-Campbell-Hausdorff formula, 97, 499
Bethe sum rule, 271
Bloch factors, 165
Bloch functions, 165
Bloch operators, 371
Bohmian mechanics, 136
Bohr magneton, 433
Bohr radius, 125
  for nuclear charge Ze, 130
Born approximation, 188
Born-Oppenheimer approximation, 356
Boson number operator, 458
Bra-ket notation, 57
Brillouin zone, 165, 369

Capture cross section, 230
Center of mass motion, 107
Charge conjugation, 429
Charge-current operators
  for the Dirac field, 428
  for the Klein-Gordon field, 416
  for the Schrödinger field, 285, 288
Christoffel symbols, 84
  in terms of metric, 89
Classical electron radius, 350
Clebsch-Gordan coefficients, 147
Coherent states, 98
  for the electromagnetic field, 329
  overcompleteness, 102
Color center, 53
  Spherical model, 135
Commutator, 76
Completeness in the mean, 494
Completeness of eigenstates, 30, 483
Completeness relations, 33
  Example with continuous and discrete states, 47
  for Fourier monomials, 164
  for free spherical waves, 123
  for hydrogen eigenstates, 134
  for spherical harmonics, 120
  for Sturm-Liouville eigenfunctions, 494
  for time-dependent Wannier states, 169
  for transfomation matrices for photon wave functions, 325

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for Wannier states, 168, 371
in cubic quantum wire, 80
in linear algebra, 61
Compton scattering, 440
Non-relativistic limit, 448
Scattering cross section, 448
Conjugate momentum, 462
Conservation laws, 276
Conserved charge, 277
Conserved current, 277
Coulomb gauge, 322
Coulomb waves, 131
Covalent bonding, 359
Covariant derivative, 257
Creation operator, 93
for non-relativistic particles, 289
for photons, 328
for relativistic fermions, 428
for relativistic scalar particles, 416

Decay rate, 223
Density of states, 199
in d dimensions, 205
in radiation, 205
in the energy scale, 204
inter-dimensional, 407
Differential scattering cross section, 233
for photons, 348
Dihydrogen cation, 356
Dimensions of states, 81
Dipole approximation, 260
Dipole line strength, 269
Dipole selection rules, 261
Dirac γ matrices, *see* γ matrices
Dirac equation, 423
Free solution, 426
Non-relativistic limit, 433
Relativistic covariance, 519
with minimal coupling, 424
Dirac picture, 210, 215
in quantum field theory, 296
Dirac's δ function, 25
Dual bases, 60

Eddington tensor, 112
Effective mass, 174
Ehrenfest's theorem, 23
Electric dipole line strength, 269
Electromagnetic coupling, 255
Electron-electron scattering, 450
Electron-photon scattering, 440
Energy-momentum tensor, 278
for classical charged particle in electromagnetic fields, 481
for quantum electrodynamics, 429
for the Maxwell field, 326
Energy-time Fourier transformation, 79
Energy-time uncertainty relation, 52, 79
Euler-Lagrange equations, 274, 462
for field theory, 274
Exchange hole, 319
Exchange integral, 308
Exchange interaction, 308

Fermi momentum, 207
Fermion number operator, 459
Fine structure constant, 444
Fock space, 289
Fourier transformation
between energy and time domain, 79
Fourier transforms, 25

Gaussian wave packet, 49
Free evolution, 49
Width, 49
Golden Rule, 226
Golden Rule #1, 228
Golden Rule #2, 229
Green's function, 48, 185
Relations between scalar and spinor Green's functions, 540
advanced, 528
for Dirac operator, 540
in d dimensions, 525
inter-dimensional, 406
retarded, 48, 185, 214, 402, 406, 528

Group, 110
Group theory, 110

Hamiltonian density
  for the Dirac field, 428
  for the Klein-Gordon field, 417
  for the Maxwell field, 326
  for the Schrödinger field, 279
Hard sphere, 190
Harmonic oscillator, 91
  Coherent states, 98
  Eigenstates, 93
    in k-representation, 95
    in x-representation, 94
  Eigenvalues, 93
  Solution by the operator method, 92
Hartree-Fock equations, 312
Heisenberg evolution equation, 214
Heisenberg picture, 210, 214
Heisenberg uncertainty relations, 75
Hellmann-Feynman theorem, 73
Hermite polynomials, 94, 497
Hermitian operator, 31
Hubbard model, 372
Hydrogen atom, 124
  bound states, 124
  ionized states, 131
Hydrogen molecule ion, 360

Induced dipole moment, 265
Interaction picture, *see* Dirac picture
Ionization rate, 223

Junction conditions for wave functions, 45

Kato cusp condition, 368
Klein's paradox, 419
Klein-Gordon equation, 414
  Non-relativistic limit, 418
  with minimal coupling, 414
Klein-Nishina cross section, 448
Kramers-Heisenberg formula, 349
Kronig-Penney model, 170

Lagrange density, 273
  for the Dirac field, 428, 520
  for the Klein-Gordon field, 415
  for the Maxwell field, 321
  for the Schrödinger field, 275
Lagrange function, 462
  for particle in electromagnetic fields, 255
  for small oscillations in N particle system, 375
Lagrangian field theory, 273
Laue conditions, 63
Liénard-Wiechert potentials, 539
Lorentz group, 111, 469
  Generators, 518
  Spinor representation, 519
    in Weyl and Dirac bases, 521
  Vector representation, 518
    Construction from the spinor representation, 522
Lorentzian absorption line, 341
Lowering operator, 93

Matrix logarithm, 503
Maxwell field, 321
Mehler formula, 96, 214, 498
Minimal coupling, 258
  in the Dirac equation, 424
  in the Klein-Gordon equation, 414
  in the Schrödinger equation, 256
  to relative motion in two-body problems, 330
Mollwo's law, 53
  Spherical model, 135
Momentum density
  for the Dirac field, 428
  for the Klein-Gordon field, 417
  for the Maxwell field, 326
  for the Schrödinger field, 279
Møller operators, 221
Møller scattering, 450

Noether's theorem, 277
Normal coordinates, 377
Normal modes, 377

Number operator, 93
for the Schrödinger field, 285
in terms of Schrödinger picture operators, 288

Occupation number operator, 93
Optical theorem, 190
Oscillator strength, 267

Parabolic coordinates, 88, 195
Passive transformation, 59
Path integrals, 241
Pauli equation, 433
Pauli matrices, 141
Pauli term, 342
Perturbation theory, 151, 209
and effective mass, 174
Time-dependent, 209
Time-independent, 151
with degeneracy, 156, 160
without degeneracy, 151, 155
Phonons, 385
Photoelectric effect, 14
Photon, 327
Photon coupling
to Dirac field, 424
to Klein-Gordon field, 414
Photon coupling to relative motion, 330
Photon flux, 340
Photon scattering, 344
Planck's radiation laws, 7
Poincaré group, 111, 469
Polar coordinates in d dimensions, 529
Polarizability tensor
Dynamic, 265
Frequency dependent, 266
Static, 263
Potential scattering, 183
Potential well, *see* Quantum well
Propagator, 48, 214

Quantization
of the Dirac field, 428
of the Klein-Gordon field, 414
of the Maxwell field, 327
of the Schrödinger field, 284
Phonons, 384
Quantum dot, 42
Quantum virial theorem, 72
Quantum well, 42
Quantum wire, 42

Raising operator, 93
Rayleigh scattering, 350
Rayleigh-Jeans law, 6
Reduced mass, 107
Reflection coefficient
for δ function potential, 46
for a square barrier, 39
for Klein' paradox, 421
Relative motion, 107
Rotation group, 110
Generators, 114
Matrix representations, 114
Rutherford scattering, 194

Scalar, 142
Scattering
Coulomb potential, 194
Hard sphere, 190
Scattering cross section, 184
for two particle collisions, 435
Scattering matrix, 221, 298
with vacuum processes divided out, 299
Schrödinger equation
Time-dependent, 18
Time-independent, 36
Schrödinger picture, 210
Schrödinger's equation, 16
Second quantization, 284
Self-adjoint operator, 30, 69
Separation of variables, 86
Shift operator, 96
Sokhotsky-Plemelj relations, 29
Sommerfeld's fine structure constant, 444
Spherical Coulomb waves, 131
Spherical harmonics, 116
Spin, 299
Spin-orbit coupling, 145

Spinor, 142
Squeezed states, 103
Stark effect, 261
Stefan-Boltzmann constant, 9
Stimulated emission, 342
Stress-energy tensor, 279
Summation convention, 58
Symmetric operator, 31
Symmetries and conservation laws, 276
Symmetry group, 110

Tensor product, 58
Thomas-Reiche-Kuhn sum rule, 268
Thomson cross section, 349, 448
Time evolution operator, 48, 211
  Two evolution operators in the interaction picture, 216
  as solution of initial value problem, 212
  Composition property, 212
  for harmonic oscillator, 213
  on states in the interaction picture, 215
  Unitarity, 213
Time ordering operator, 211
Tonomura experiment, 21
Transition frequency, 220
Transition probability, 220
Transmission coefficient
  for δ function potential, 46
  for a square barrier, 39
  for Klein' paradox, 421
Transverse δ function, 325
Tunnel effect, 40
Two-particle state, 300
Two-particle system, 107

Uncertainty relations, 75
Unitary operator, 70

Vector, 142
Vector addition coefficients, 147
Virial theorem, 71

Wannier operators, 371
Wannier states, 167
  Completeness relations, 168
  Time-dependent, 169
Wave packets, 47
Wave-particle duality, 15
Wien's displacement law, 5

Yukawa potentials, 399